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(54) COMPOSITION FOR TREATING KERATINOUS MATERIALS CONSISTING OF A CATIONIC POLY(ALKYL) VINYLLACTUM POLYMER AND A PROTECTING OR CONDITIONING AGENT

(57) Abstract: The invention concerns a composition for treating keratinous materials, in particular hair, comprising, in a physiologically and in particular cosmetically acceptable medium, at least a protecting and conditioning agent, and additionally at least a cationic poly(alkyl) vinyllactam polymer. Said combinations enable to improve deposition of the agent protecting or conditioning the keratinous materials and the cosmetic properties.

The invention concerns a composition for treating keratinous materials, in particular human keratinous fibers such as hair, consisting of, in a physiologically and in particular a cosmetically acceptable medium, at least a protecting and conditioning agent, and additionally at

least a cationic poly(alkyl) vinyllactam polymer.

Such combinations make it possible to improve deposition of the agent protecting or conditioning the keratinous material and the cosmetic properties.

It is well known that hair is sensitive or weakened to varying degrees by atmospheric agents, and in particular by light, water, and humidity, as well as by the repeated action of different capillary treatments such as washing, permanents, straightening, dying, and bleaching. Numerous studies have shown that natural light destroys certain amino acids in hair. Such assaults alter the capillary fiber, reducing its mechanical properties such as resistance to traction, breaking load and elasticity, or its resistance to swelling in an aqueous medium. Hair then becomes dull, coarse, and brittle. And contrary to skin, hair becomes lighter in color.

It is also known that light and washing agents, in particular, have a tendency to attack the natural color of the hair as well as the artificial color of dyed hair. The color of the hair weakens little by little or veers toward unattractive or undesirable shades.

For many years, the cosmetic industry has been searching for substances that will protect the hair from degradation caused by atmospheric attacks, such as light and heat and various treatments. In particular, it has been looking for products to protect naturally colored or artificially dyed keratinous fibers while preserving or strengthening the intrinsic mechanical properties of keratinous fibers (resistance to traction, breaking load and elasticity, or their resistance to swelling in an aqueous environment).

To combat such degradations to the keratin in hair, it has already been suggested that certain substances be used which are capable of filtering light rays, such as 2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid or its salts (FR-A- 2 627 085) or 4-(2-oxo-3-bornylidine methyl) benzene sulfonic acid or its salts (EP-A-329 032), or also lactoferrin (FR-A-2 673 839).

However, when such filters are effective, it is only at very high concentrations. Now, at such concentrations, the treated hair feels very dull and heavy. In addition, it is very difficult to untangle.

It has already been suggested that conditioning agents be used in compositions for shampoos or care products for keratinous materials such as hair, and in particular cationic polymers or silicones to facilitate untangling the hair and to give it softness and suppleness. However, the abovementioned cosmetic advantages are also unfortunately accompanied by certain cosmetic effects that, in dry hair, are considered undesirable, namely weighing down the hair (lack of lightness to the hair), or a lack of smoothness (hair that is not homogenous from root to tip).

In addition, the use of cationic polymers for this purpose has a number of disadvantages. Given their strong affinity to hair, some of these polymers cause major build-up after repeated use, and lead to undesirable effects such as an unpleasant feel, heaviness, stiffness of the hair, and inter-fiber cohesion that affects styling. These effects are accentuated in the case of fine hair, which lacks body and volume.

It is well known that hair that has been sensitized (i.e. damaged and/or weakened) to various degrees by the action of atmospheric agents or by the action of mechanical or chemical treatments, such as dyes, bleaches, and/or permanents, is often difficult to untangle and style, and lacks softness.

In short, it is clear that current cosmetic compositions containing protective or conditioning agents do not provide full satisfaction.

The applicant has not discovered that the combination of a specific cationic poly(alkyl) vinyllactam polymer with protective or conditioning agents may remedy these disadvantages.

So, at the end of significant research into the subject, the applicant has now discovered that by introducing a specific polymer into compositions, and particularly capillary compositions based on agents protecting or conditioning keratinous materials, it is possible to increase deposition of the agent protecting or conditioning the keratinous material and by the same means increase protection or conditioning.

While not wishing to limit this invention to any one theory, it seemed that during the rinse stage there were particular interactions and/or affinities between the agent protecting or conditioning the keratinous material, the poly(alkyl) vinyllactam polymers according to the invention, and the hair, which promoted a uniform, significant, and lasting deposit of the agent protecting or conditioning the keratinous material and the poly(alkyl) vinyllactam polymers onto the surface of said hair, this qualitative and quantitative deposit probably being one of the causes for the improvement observed in terms of ultimate properties, in particular ease of styling, maintenance, body, and volume of the treated hair. All these discoveries are the basis for this invention.

So, according to the invention, new cosmetic compositions are now being proposed, consisting of, in a physiologically and in particular cosmetically acceptable medium, at least one agent protecting or conditioning the keratinous materials and at least one cationic poly(alkyl) vinyllactam polymer consisting of:

- a) at least one vinyllactam or alkyl(C<sub>1</sub>-C<sub>5</sub>) vinyllactam type monomer
- b) at least one monomer chosen from among those with structures (I) and (II):

$$CH_{2}^{-}C(R_{1})-CO-X-(Y)_{p}^{-}(CH_{2}^{-}CH_{2}^{-}O)_{m}^{-}(CH_{2}^{-}CH(R_{2}^{-}O)_{n}^{-}(Y_{1}^{-})_{q}^{-}N_{1}^{-}R_{4}^{-}$$

$$(1) \qquad Z^{-}R_{5}^{-}$$

$$CH_{2}^{-}C(R_{1})-CO-X-(Y)_{p}^{-}(CH_{2}-CH_{2}-O)_{m}^{-}(CH_{2}-CH(R_{2})-O)_{n}^{-}(Y_{1})_{q}^{-}-N \\ R_{4}$$
(II)

where:

X designates an atom of oxygen or a radical NR<sub>6</sub>,

 $R_1$  and  $R_6$  each independently designates either an atom of hydrogen or a linear or branched alkyl radical composed of  $C_1$ - $C_5$ ,

R<sub>2</sub> designates a linear or branched alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>,

 $R_3$ ,  $R_4$ , and  $R_5$  each independently designates an atom of hydrogen, a linear or branched alkyl radical composed of  $C_1$ - $C_{30}$  or a radical from formula (III):

$$--(Y_2)_7 - (CH_2 - CH(R_7) - O)_x - R_8$$
 (III)

Y,  $Y_1$ , and  $Y_2$  each independently designates a linear or branched alkylene radical composed of  $C_2$ - $C_{16}$ .

 $R_7$  designates hydrogen, a linear or branched alkyl radical composed of  $C_1$ - $C_4$ , or a linear or branched hydroxy alkyl radical composed of  $C_1$ - $C_4$ .

R<sub>8</sub> designates an atom of hydrogen or a linear or branched alkyl radical composed of C<sub>1</sub>-C<sub>30</sub>, p, q, and r each independently designates either the value 0 or the value 1, m and n each independently designate a whole number between 0 and 100, x designates a whole number from 1 to 100, Z designates an ion of organic or mineral acid,

## provided that:

- at least one of the substituent R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, or R<sub>8</sub> designates a linear or branched alkyl radical composed of C<sub>9</sub>-C<sub>30</sub>,
  - if m or n are not equal to 0, then q is equal to 1,
  - if m or n are equal to 0, then either p or q is equal to 0.

Another purpose of the invention concerns the use of at least one cationic poly(alkyl) vinyllactam polymer in, or for the manufacture of, a cosmetic composition consisting of a protecting or conditioning agent of keratinous material.

It is also the purpose of the invention to use at least one cationic poly(alkyl) vinyllactam polymer in a composition consisting of a protective agent for keratinous materials to improve the effectiveness of such protecting or conditioning agent for keratinous materials.

It is also a goal of the invention to use at least one cationic poly(alkyl) vinyllactam polymer in a composition consisting of a protecting or conditioning agent for keratinous materials to improve the deposition and/or fixing of such protective agent to the keratinous material.

The various purposes of the invention will now be described. The set of meanings and definitions of the compounds used in the invention as set forth below are valid for all purposes of the invention.

While not wishing to be bound by any one theory, it seemed that the advantages provided by the polymers of the invention are related to the behavior of associative types of thickening polymers.

Associative polymers are polymers where the molecules are able, in the formation medium, to combine with each other or with molecules of other compounds.

Their chemical structure generally comprises at least one hydrophilic area and at least one hydrophobic area, the hydrophobic areas consisting of at least one fatty chain.

The cationic poly(alkyl) vinyllactam polymers according to the invention comprise:

- a) at least one vinyllactam or alkyl $(C_1-C_5)$  vinyllactam type monomer,
- b) at least one monomer chosen from among those with structures (I) and (II)

$$CH_{2}^{-}C(R_{1})-CO-X-(Y)_{p}^{-}(CH_{2}\cdot CH_{2}\cdot O)_{m}^{-}(CH_{2}\cdot CH(R_{2})\cdot O)_{n}^{-}(Y_{1})_{q}^{-}-N \xrightarrow{R_{3}} (II)$$

where:

X designates an atom of oxygen or a radical NR<sub>6</sub>,

 $R_1$  and  $R_6$  each independently designates either an atom of hydrogen or a linear or branched alkyl radical composed of  $C_1$ - $C_5$ ,

 $R_2$  designates a linear or branched alkyl radical composed of  $C_1\text{-}C_4$ ,

 $R_3$ ,  $R_4$ , and  $R_5$  each independently designates an atom of hydrogen, a linear or branched alkyl radical composed of  $C_1$ - $C_{30}$  or a radical from formula (III):

$$--(Y_2)_r - (CH_2 - CH(R_7) - O)_x - R_8$$
 (III)

Y,  $Y_1$ , and  $Y_2$  each independently designates a linear or branched alkylene radical composed of  $C_2$ - $C_{16}$ .

R<sub>7</sub> designates hydrogen, a linear or branched alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>, or a linear or

branched hydroxy alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>.

R<sub>8</sub> designates hydrogen or a linear or branched alkyl radical composed of C<sub>1</sub>-C<sub>30</sub>, p, q, and r each independently designates either the value 0 or the value 1, m and n each independently designate a whole number between 0 and 100, x designates a whole number from 1 to 100, Z designates an ion of organic or mineral acid, provided that:

- at least one of the substituent  $R_3$ ,  $R_4$ ,  $R_5$ , or  $R_8$  designates a linear or branched alkyl radical composed of  $C_9$ - $C_{30}$ ,
  - if m or n are not equal to 0, then q is equal to 1,
  - if m or n are equal to 0, then either p or q is equal to 0.

The polymers according to the invention may be reticulated or not and may also be block polymers.

Preferably, counter ion Z- of the monomers of formula (I) is chosen from among halogenous ions, phosphate ions, the methosulfate ion, or tosylate ion.

Preferably,  $R_3$ ,  $R_4$ , and  $R_5$  in formulas (I) and/or (II) each independently designates an atom of hydrogen or a linear or branched alkyl radical composed of  $C_1$ - $C_{30}$ .

More preferably, monomer b) is a monomer from formula (I), and even more preferably, m and n are equal to 0.

The vinyllactam or alkyl vinyllactam monomer is preferably a compound with structure (IV):

$$CH(R_9) = C(R_{10}) - N = O$$

$$(CH_2)_8$$

where:

s designates a whole number between 3 and 6,

R<sub>9</sub> designates an atom of hydrogen or an alkyl radical composed of C<sub>1</sub>-C<sub>5</sub>,

R<sub>10</sub> designates an atom of hydrogen or an alkyl radical composed of C<sub>1</sub>-C<sub>5</sub>,

Provided that at least one of radicals R<sub>9</sub> and R<sub>10</sub> designates an atom of hydrogen.

Even more preferably, monomer (IV) is vinylpyrrolidone.

The polymers according to the invention may also contain one or more additional monomers, preferably cationic or non-ionic.

Of the compounds more specifically preferred, we can cite the terpolymers consisting of at least:

- a) one formula (IV) monomer.
- b) one formula (I) monomer in which p=1, q=0, R<sub>3</sub> and R<sub>4</sub> designate a hydrogen atom or an alkyl radical composed of C<sub>1</sub>-C<sub>5</sub>, and R<sub>5</sub> designates an alkyl radical composed of C<sub>9</sub>-C<sub>24</sub>, m and n are zero, and
- c) one formula (II) monomer in which R<sub>3</sub> and R<sub>4</sub> designate a hydrogen atom or an alkyl radical composed of C<sub>1</sub>-C<sub>5</sub>, and m and n are zero.

Even more preferentially, poly(alkyl) vinyllactam terpolymers are used, consisting of 40 to 95% by weight of monomer (a), 25 to 50% of monomer (b), and 0.1 to 55% of monomer (c).

These polymers are described in Patent pending WO 00/68282, the content of which forms an integral part of this invention.

As cationic poly(alkyl) vinyllactam polymers according to the invention, in particular it is possible to use the vinyl pyrrolidone terpolymers / dimethyl amino propyl methacrylamide / dodecyl dimethyl methacrylamidopropyl ammonium tosylate, the vinyl pyrrolidone terpolymers / dimethyl amino propyl methacrylamide / cocoyl dimethyl methacrylamidopropyl ammonium tosylate, the vinyl pyrrolidone terpolymers / dimethyl amino propyl methacrylamide / lauryl dimethyl methacrylamidopropyl ammonium tosylate or chloride.

The molecular weight by weight of the cationic polymers of the invention is preferably comprised between 500 and 20,000,000. More specifically, it is comprised between 200,000 and 2,000,000, and even more specifically comprised between 400,000 and 800,000.

The cationic poly(alkyl) vinyllactam polymers are preferably used in a quantity that may range from about 0.01 to 10% by weight of the total weight of the composition for treating keratinous materials. More preferentially, this amount ranges from about 0.1 to 5% by weight.

The agents protecting the keratinous materials may also be any active agent used to prevent or limit the degrading effects of physical or chemical assaults.

So, the agents protecting the keratinous materials may chosen from among hydrosoluble, liposoluble, and water-insoluble organic UV filters, antiradical agents, antioxidants, vitamins, or pro-vitamins.

Organic UV filters (systems that filter out UV rays) are in particular chosen from among hydrosoluble or liposoluble filters, whether siliconated or nonsiliconated, and mineral oxide nanoparticles, the surface of which may eventually be treated to make them hydrophilic or hydrophobic.

Hydrosoluble organic UV filters may be chosen, for example, from among para-amino benzoic acid and its salts, anthranilic acid and its salts, salicylic acid and its salts, hydroxy

cinnamic acid and its salts, sulfonic derivatives of benz-x-axole (benzothiazols, benzimidizols, benzoxazols) and their salts, sulfonic derivatives of benzophenone and their salts, sulfonic derivatives of benzylidene camphor and their salts, the derivatives of benzylidene camphor substituted by a quaternary amine and their salts, derivatives of phthalydene-camphosulfonic acids and their salts, sulfonic derivatives of benzotriazol, and mixtures of them.

It is also possible to use hydrophilic polymers which, additionally and because of their chemical nature, have light-protective qualities against UV rays. These include polymers consisting of benzylidene camphor and/or benzotriazol groups, substituted by quaternary sulfonic or ammonium groups.

Of the liposoluble (or lipophilic) organic UV filters appropriate for use in the invention, we can cite in particular: derivatives of para-aminobenzoic acid, such as the esters or amides of para-aminobenzoic acid; derivatives of salicylic acid such as the esters; derivatives of benzophenone; derivatives of dibenzoyl methane; derivatives of diphenyl acrylates; derivatives of benzofurans; UV filter polymers containing one or more silico-organic residues; esters of cinnamic acid; derivatives of camphor; derivatives of trianilino-s-triazine; the ethylic ester urocanic acid; benzotriazols; derivatives of hydroxy phenyl triazine; bis-resocinol-dialkyl amino triazine; and mixtures of them.

The liposoluble (or lipophilic) organic UV filter according to the invention is preferably chosen from among: octyl salicylate; 4-tert-butyl-4'-methoxy dibenzoyl methane (GIVAUDAN's PARSOL 1789); octocrylene; 4-methoxy cinnamate of 2-ethylhexyl [2-ethylhexyl 4-methoxycinnamate] (PARSOL MCX), and the compound from the following formula (V), or 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethyl silyl)oxy] disiloxanyl]propynyl]phenol, as described in Patent pending EP-A-0 392 883:

Other UV filters particularly preferred according to the invention are derivatives of benzophenones such as UNINUL MS 40 (2-hydroxy-4-methoxy benzophenone-5-sulfonic acid) and UNINUL M40 (2-hydroxy 4-methoxy benzophenone) marketed by BASF, derivatives of benzalmalonates such as PARSOL SLX (poly dimethyl/methyl (3(4-(2,2-bis-ethoxy carbonyl vinyl)-phenoxy)-propenyl) siloxane) marketed by GIVAUDAN-ROURE, derivatives of benzylidene camphor such as MEXORYL SX (b-b'camphosulfonic [1-4 divinylbenzene] acid) manufactured by the firm CHIMEX, derivatives of benzimidazole such as EUSOLEX 232 (2-phenyl-benzimidazol-5-sulfonic acid) marketed by MERCK.

The mineral oxides may be selected from among titanium oxides, zinc oxides, and cerium oxides.

The antioxidants or antiradical agents are in particular selected from among the phenols such as BHA (tert-butyl-4-hydroxy anisole), BHT (2,6-di-tert-butyl-p-cresol), TBHQ (tert-butyl hydroquinone), the polyphenols such as the proanthocyanodic oligomers and the flavonoids, the hindered amines known by the generic term HALS (Hindered Amine Light Stabilizer) such as tetra amino piperidine, erythorbic acid, the polyamines such as spermine, cysteine, glutathione, superoxide dismutase, and lactoferrin.

The vitamins are in particular chosen from among ascorbic acid, vitamin E, vitamin E acetate, the B vitamins such as B3 and B5, vitamin PP, vitamin A, and their derivatives.

The provitamins are in particular chosen from between panthenol and retinol.

The sequestrants are in particular chosen from between DEQUEST, such as diethylene triamine pentamethylene phosphonic acid and diethylene triamine tetramethylene phosphonic acid and their salts, and EDTA (ethylenediaminetetra-acetic acid) and its salts, particularly sodium or potassium.

According to the invention, the agent or agents protecting the keratinous material may represent from 0.001% to 20% by weight, and preferably from 0.01% to 10% by weight, and more specifically 0.1 to 5% by weight in relation to the total weight of the final composition.

Within the context of this application, a conditioning agent is understood to be any agent the function of which is to improve the cosmetic properties of the hair, particularly softness, untangling, feel, and static electricity.

Conditioning agents may be in liquid, semi-solid, or solid form such as oils, waxes, or gums.

According to the invention, conditioning agents may be chosen from among the synthesis oils such as polyolefins, mineral oils, vegetable oils, fluoridated or perfluoridated oils, natural or synthetic waxes, silicones, cationic polymers, ceramide type compounds, cationic surfactants, fatty amines, fatty acids and their derivatives, as well as mixtures of these different compounds.

The preferred conditioning agents according to the invention are the cationic polymers and silicones.

The synthesis oils are polyolefins and particularly poly- $\alpha$ -olefins, and more specifically:

- the polybutene type, hydrogenated or not, and preferably polyisobutene, hydrogenated or not.

It is preferable to use isobutylene oligomers with a molecular weight of less than 1000

and a mixture of them with polyisobutylenes having a molecular weight that is greater than 1000, and preferably comprised between 1000 and 15,000.

As examples of the poly- $\alpha$ -olefins that are usable within the context of the invention, we can mention very specifically the polyisobutenes sold under the name PERMETHYL 99A, 101A, 102A 104A (n = 16), and 106A (n = 38) by the corporation PRESPERSE Inc., or the products sold under the name ARLAMOL HD (n = 3) by the ICI corporation (with n designating the degree of polymerization),

- the polydecene type, whether hydrogenated or not.

These products are sold, for example, under the names ETHYLFLO by the corporation ETHYL CORP. and ARLAMOL PAO by the ICI corporation.

The mineral oils suitable for use in the compositions of the invention are preferentially selected from among the group comprised of:

- hydrocarbons, such as hexadecane and oil of paraffin;

The animal and vegetable oils are preferentially chosen from the group that includes sunflower, corn, soy, avocado, jojoba, squash, raisin seed, sesame seed, and walnut oils, fish oils, glycerol tricaprocaprylate, or vegetable or animal oils of the formula R<sub>9</sub>COOR<sub>10</sub> where R<sub>9</sub> represents the remnant of a higher fatty acid containing from 7 to 29 carbon atoms and R<sub>10</sub> represents a linear or branched hydrocarbon chain containing from 3 to 30 carbon atoms, specifically alkyl or alkenyl, for example, Purcellin oil or liquid jojoba wax;

It is also possible to use natural or synthetic essential oils such as, for example, eucalyptus, lavender, vetiver, litsea cubeba, lemon, sandalwood, rosemary, chamomile, savory, nutmeg, cinnamon, hyssop, caraway, orange, geranium, cade, and bergamot;

Waxes are natural (animal or vegetable) or synthetic substances that are solid at room

temperature (20-25°C). They are insoluble in water, soluble in oils, and are capable of forming a water-repellent film.

For a definition of waxes, we can cite, for example, P.D. Dorgan, Drug and Cosmetic Industry, December 1983, pages 30-33.

The chosen wax or waxes are among, in particular, carnauba wax, candelila wax, alfa wax, paraffin wax, ozokerite, vegetable waxes such as olive wax, rice wax, hydrogenated jojoba wax, or absolute flower waxes such as black currant flower essential wax sold by the BERTIN corporation (France), animal waxes such as bees wax, or modified bees wax (cerabellina); other waxes or waxy raw materials that can be used according to the invention are in particular marine waxes such as those sold by the SOPHIM firm under reference M82, and polyethylene or polyolefin waxes in general.

The cationic polymers (other than the poly (alkyl) vinyllactam polymers according to the invention) that may be used according to the invention may be chosen from among those that are already known to improve the cosmetic properties of hair treated by detergent compositions, namely those described in Patent pending EP-A 0 337 354 and in French Patents pending FR-A 2 270 846, 2 383 660, 2 598 611, 2 470 596, and 2 519 863.

More generally, the expression "cationic polymer" as it is used in the invention, indicates any polymer containing cationic groups and/or ionizable groups in cationic groups.

The preferred cationic polymers are chosen from among those containing units including primary, secondary, tertiary, and/or quaternary amine groups that may either form part of the main polymer chain, or are carried on a substituent lateral directly connected to it.

The cationic polymers used generally have a molecular weight the average number of which falls between about 500 and 5•10<sup>6</sup>, and preferably falls between about 10<sup>3</sup> and 3•10<sup>6</sup>.

Among the cationic polymers, it is possible to cite in particular the polyamine, polyaminoamide, and quaternary polyammonium types of polymers. These are known products.

Among the polyamine, polyaminoamide, and quaternary polyammonium types of polymers that are suitable for use according to the invention, we can mention in particular those described in French Patents Nos. 2 505 348 and 2 542 997. Among these polymers it is worth mentioning:

(1) the homopolymers and copolymers derived from acrylic or methacrylic esters or amides and consisting of at least one of the following formula units:

where:

R<sub>1</sub> and R<sub>2</sub>, whether identical or different, represent hydrogen or an alkyl group having 1 to 6 atoms of carbon, and preferably methyl or ethyl;

R<sub>3</sub>, whether identical or different, designate an atom of hydrogen or a radical CH<sub>3</sub>;

A, whether identical or different, represent an alkyl group, linear or branched, of 1 to 6

carbon atoms, preferably 2 or 3 carbon atoms, or a hydroxy alkyl group of 1 to 4 carbon atoms;

R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub>, whether identical or different, represent an alkyl group having 1 to 18 atoms of carbon or a benzyl radical, and preferably an alkyl group having from 1 to 6 carbon atoms;

X designates an anion derived from a mineral or organic acid, such as methosulfate or a halogenide anion such as chloride or bromide.

The copolymers of family (1) may additionally contain one or more units deriving from comonomers that may be chosen from among the family of acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides in which the nitrogen is substituted by lower alkyls (C1-C4), acrylic or methacrylic acids or their esters, vinyllactams such as vinyl pyrrolidone or vinyl caprolactam, and vinylic esters.

So, among the copolymers of family (1) we can cite:

- copolymers of acrylamide and dimethyl amino ethyl methacrylate quaternized with dimethyl sulfate or with dimethyl halogenide such as the one sold under the name HERCOFLOC by the HERCULES corporation,
- copolymers of acrylamide and methacryloyl oxyethyl trimethyl ammonium chloride, described for example in Patent pending EP-A-080976 and sold under the name BINA QUAT P 100 by the corporation CIBA GEIGY,
- the copolymer of acrylamide and methacryloyl oxyethyl trimethyl ammonium methosulfate sold under the name RETEN by the HERCULES corporation,
- colpolymers of vinyl pyrrolidone / dialkyl amino alkyl acrylate or methacrylate, whether quaternized or not, such as the products sold under the name "GAFQUAT" by the ISP corporation, such as "GAFQUAT 743," for example, or "GAFQUAT 755," or the products

known as "COPOLYMER 845, 958, and 937." These polymers are described in detail in French Patents 2,077,143 and 2,393,573,

- the dimethyl amino ethyl methacrylate / vinyl caprolactam / vinyl pyrrolidone terpolymers, such as the product sold under the name GAFFIX VC 713 by the ISP corporation,
- the vinyl pyrrolidone / methacrylamidopropyl dimethylamine copolymer, marketed in particular under the name STYLEZE CC 10 by ISP,
- and the vinyl pyrrolidone / quaternized dimethyl amino propyl methacrylamide copolymers such as the product sold under the name "GAFQUAT HS 100" by the ISP corporation.
- (2) Derivatives of cellulose ethers including quaternary ammonium groups described in French Patent 1,492,597, and in particular the copolymers marketed under the names "JR" (JR 400, JR 125, JR 30M) or "LR" (LR 400, LR 30M) by the Union Carbide Corporation. These polymers are also defined in the CTFA dictionary as hydroxy ethyl cellulose quaternary ammonium that have reacted with an epoxide substituted by a trimethyl ammonium group.
- (3) Derivatives of cationic cellulose such as cellulose copolymers or derivatives of cellulose grafted with a hydrosoluble quaternary ammonium monomer, and described specifically in Patent US 4,131,576, such as the hydroxy alkyl cellulose, and the hydroxy methyl-, hydroxy ethyl- or hydroxy propyl cellulose grafted specifically with a salt of methacryloyl ethyl trimethyl ammonium, methacrylamidopropyl trimethyl ammonium, or dimethyl diallyl ammonium.

The commercial products that correspond to that definition are in particular the products sold under the name "Celquat L 200" and "Celquat H 100" by the National Starch corporation.

(4) Cationic polysaccharides described specifically in US Patents 3,589,578 and

4,031,307, such as guar gums containing cationic trialkyl ammonium groups. It is possible to use, for example, guar gums modified by a salt (chloride, for instance) of 2,3-epoxy propyl trimethyl ammonium.

Products of this kind are marketed, specifically, under the brand names JAGUAR C13 S, JAGUAR C 15, JAGUAR C 17, or JAGUAR C 162 by the MEYHALL corporation.

- (5) polymers composed of piperazinyl units and alkylene or hydroxy alkylene divalent radicals with straight or branched chains, possibly interrupted by atoms of oxygen, sulfur, nitrogen, or by aromatic or heterocyclic cycles, as well as the products of the oxidation and/or quaternization of such polymers. These polymers are described, in particular, in French Patents 2,162,025 and 2,280,361;
- (6) water-soluble polyamino amides prepared, in particular, by polycondensation of an acid compound with a polyamine; these polyamino amides may be reticulated by an epihalohydrine, a diepoxide, a dianhydride, an unsaturated dianhydride, a bis-unsaturated derivative, bis-halohydrine, bis-azetidinium, bis-haloacyl diamine, alkyl bis-halogenide, or even by an oligomer resulting from the reaction of a bi-functional reagent vis-a-vis a bis-halohydrine, bis-azetidinium, bis-haloacyl diamine, alkyl bis-halogenide, epihalohydrine, diepoxide, or an unsaturated derivative; the reticulating agent being used in proportions ranging from 0.025 to 0.35 mole per amine group of the polyamino amide; these polyamino amides may be alcoyl or, if they include one or more tertiary amine functions, quaternized. Such polymers are described in particular in French Patents 2,252,840 and 2,368,508;
- (7) derivatives of polyamino amides resulting from the condensation of polyalcoylene polyamines with polycarboxylic acids followed by alcoylation by bi-functional agents. We can cite, for example, adipic-dialcoyl amino hydroxyl alcoyl dialoylene triaminic acid polymers in

which the alcoyl radical comprises 1 to 4 atoms of carbon and preferably designates methyl, ethyl, or propyl. Such polymers are described in particular in French Patent 1,583,363.

Among such derivatives, we can cite in particular the adipic/dimethyl amino hydroxy propyl/diethylene triaminic acid polymers sold under the name "Cartaretine F, F4, or F8" by the Sandoz firm.

(8) polymers obtained by reaction of a polyalkylene polyamine containing two primary amine groups and at least one secondary amine group with a dioxycarboxylic acid chosen from among diglycolic acid and saturated dicarboxylic aliphatic acids having 3 to 8 atoms of carbon. The molar ratio between the polyalkylene polyamine and the dicarboxylic acid being between 0.8:1 and 1.4:1; the polyaminoamide resulting from it being caused to react with epichlorhydrine in a molar ratio of epichlorhydrine to the secondary amine group of the polyaminoamide comprised between 0.5:1 and 1.8:1. These polymers are described in particular in US Patents 3,227,615 and 2,961,347.

Polymers of this kind are marketed in particular under the name "Hercosett 57" by the firm Hercules Inc., or under the name "PD 170" or "Delsette 101" by the Hercules corporation in the case of the adipic acid / epoxypropyl / diethylene triamine copolymer.

(9) the cyclopolymers of alkyl dialyl amine or dialkyl dialyl ammonium such as homopolymers or copolymers consisting of as the primary constituent of the chain units that meet the following formulas (X) or (XI):

$$-(CH_{2})t - CR_{12} CH_{2} CH_{2} - (CH_{2})k CH_{2} - (CH_{2})t - CR_{12} CH_{2} CH_{2} - (CH_{2})t - CH_{2} C$$

formulas in which k and t are equal to 0 or 1, the sum of k + t being equal to 1;  $R_{12}$  designates an atom of hydrogen or a methyl radical;  $R_{10}$  and  $R_{11}$  each independently designates a alkyl group with from 1 to 22 atoms of carbon, a hydroxy alkyl group in which the alkyl group preferably has 1 to 5 carbon atoms, a lower amidoalkyl group (C1-C4), or  $R_{10}$  and  $R_{11}$  may jointly designate with the nitrogen atom to which they are linked, heterocyclic groups, such as piperidine or morpholinyl; Y is an anion such as bromide, chloride, acetate, borate, citrate, tartrate, bisulfate, bisulfate, or phosphate. These polymers are described in particular in French Patent 2,080,759 and in its certificate of addition 2,190,406.

 $R_{10}$  and  $R_{11}$  designate independently from one another preferably an alkyl group having from 1 to 4 carbon atoms.

Among the polymers defined above, we can cite most particularly the homopolymer of dimethyl diallyl ammonium chloride sold under the name "Merquat 100" by the Calgon company (and others like it with low average molecular weight by weight) and copolymers of diallyl dimethyl ammonium chloride and acrylamide marketed under the name "MERQUAT 550."

(10) the quaternary diammonium polymer containing recurrent units that correspond to the formula:

formula (XII) in which:

 $R_{13}$ ,  $R_{14}$ ,  $R_{15}$ , and  $R_{16}$ , whether identical or different, represent aliphatic, alicyclic, or aryl- aliphatic radicals containing 1 to 20 carbon atoms or lower hydroxy alkyl aliphatic radicals,

or R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, and R<sub>16</sub>, whether jointly or separately, constitute heterocycles with the nitrogen atoms to which they are attached, eventually containing a second heteroatom other than nitrogen, or R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, and R<sub>16</sub> represent a linear or branched alkyl radical composed of C1-C6 substituted by a nitrile, ester, acyl, amide or to CO-O-R<sub>17</sub>-D, or CO-NH-R<sub>17</sub>-D group, where R<sub>17</sub> is an alkylene and D a quaternary ammonium group;

A1 and B1 represent polymethylenic groups containing 2 to 20 carbon atoms that may be linear or branched, saturated or unsaturated, and may contain one or more aromatic cycles linked to or inserted in the main chain, or one or more atoms of oxygen, sulfur, or sulfoxide, sulfone, disulfur, amino, alkyl amino, hydroxyl, quaternary ammonium, ureide, amide, or ester groups; and

X designates an anion derived from a mineral or organic acid;

A1, R<sub>13</sub>, and R<sub>15</sub> may form a piperazinic cycle with the two nitrogen atoms to which they are attached; in addition, if A1 designates a linear or branched, saturated or unsaturated alkylene or hydroxy alkylene radical, then B1 may also designate a (CH<sub>2</sub>)n-CO-D-OC-(CH<sub>2</sub>)n-group:

where D designates:

a) a glycol residue of the formula: -O-Z-O-, where Z designates a linear or branched hydrocarbon radical or a group that corresponds to one of the following formulas:

where x and y designate a whole number between 1 and 4, representing a defined and unique degree of polymerization or any number from 1 to 4 representing an average degree of polymerization;

- b) a bis-secondary diamine remnant such as a piperazine derivative;
- c) a bis-primary diamine remnant of the formula: -NH-Y-NH-, where Y designates a linear or branched hydrocarbon radical, or the bivalent radical

#### -CH2-CH2-S-S-CH2-CH2-;

d) a ureylene group of the formula: -NH-CO-NH-;

X is preferably an anion such as chloride or bromide.

These polymers have a number-average molecular weight between 1000 and 10,000.

Polymers of this type are described particularly in French Patents 2,320,330, 2,270,846, 2,316,271, 2,336,434, and 2,413,907, and in US Patents 2,273,780, 2,375,853, 2,388,614, 2,454,547, 3,206,462, 2,261,002, 2,271,378, 3,874,870, 4,001,432, 3,929,990, 3,966,904, 4,005,193, 4,025,617, 4,025,627, 4,025,653, 4,026,945, and 4,027,020.

In particular, it is possible to use polymers composed of recurrent units corresponding to the formula:

where  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$ , whether identical or different, designate an alkyl or hydroxy alkyl radical having above 1 to 4 carbon atoms, n and p are whole numbers from about 2 to 20, and  $X^-$  is an anion derived from a mineral or organic acid.

A particularly preferred compound of formula (a) is one in which  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  represent a methyl radical and n = 3, p = 6, and X = Cl, known as Hexadimethrine chloride according to the INCI (CTFA) nomenclature.

(11) quaternary polyammonium polymers consisting of units of formula (XIII):

a formula in which:

 $R_{18}$ ,  $R_{19}$ ,  $R_{20}$ , and  $R_{21}$ , whether identical or different, represent an atom of hydrogen or a methyl, ethyl, propyl,  $\beta$ -hydroxy ethyl,  $\beta$ -hydroxy propyl, or to  $CH_2CH_2(OCH_2CH_2)pOH$  radical,

where p is equal to 0 or to a whole number between 1 and 6, provided that  $R_{18}$ ,  $R_{19}$ ,  $R_{20}$ , and  $R_{21}$  do not simultaneously represent an atom of hydrogen,

r and s, whether identical or different, are whole numbers between 1 and 6, q is equal to 0 or to a whole number between 1 and 34,

X designates a halide,

A designates a dihalide radical or preferably represents to CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-.

These compounds are described in particular in Patent pending EP-A-122,324.

Among them, it is worth mentioning the "Mirapol® A 15", "Mirapol® AD1", "Mirapol® AZ1", and "Mirapol® 175" products sold by the Miranol firm.

- (12) The quaternary polymers of vinyl pyrrolidone and vinyl imidazole such as the products sold under the names Luviquat® FC 905, FC 550, and FC 370 by the B.A.S.F. company.
- (13) Quaternary polyamines such as Polyquart® H sold by HENKEL, and referenced under the name "POLYETHYLENE GLYCOL (15) TALLOW POLYAMINE" in the CTFA dictionary.
  - (14) Reticulated polymers of salts of methacryloyloxy alkyl(C1-C4) trialkyl(C1-C4)

ammonium, such as the polymers obtained by homopolymerization of dimethyl amino ethyl methacrylate quaternized by methyl chloride, or by copolymerization of acrylamide with dimethyl amino ethyl methacrylate quaternized by methyl chloride, the homo- or copolymerization being followed by reticulation by a compound with olefinic unsaturation, in particular methylene bis acrylamide. In particular it is possible to use an acrylamide / methacryloyloxy ethyl trimethyl ammonium chloride reticulated copolymer, (20/80) by weight, in the form of a dispersion containing 50% by weight of said polymer in mineral oil. This dispersion is marketed under the name "SALCARE® SC 92" by the ALLIED COLLOIDS company. It is also possible to use a reticulated homopolymer of methacryloyloxy ethyl trimethyl ammonium chloride containing about 50% by weight of the homopolymer in mineral oil or in a liquid ester. These dispersions are marketed under the names "SALCARE® SC 95" and "SALCARE® SC 96" by the ALLIED COLLOIDS company.

Other cationic polymers that may be used within the context of the invention are cationic proteins or hydrolyzed cationic proteins, polyalykleneimines, and in particular the polyethyleneimines, polymers containing vinyl pyridine or vinyl pyridinium units, condensates of polyamines and epichlorhydrines, quaternary polyureylenes, and derivatives of chitine.

Among all the cationic polymers that are suitable for use within the context of the invention, the preferred ones are derivatives of quaternary cellulose ethers, such as the products sold under the name "JR 400" by UNION CARBIDE CORPORATION, the cationic cyclopolymers, specifically the homopolymers and copolymers of dimethyl diallyl ammonium chloride, sold under the names "MERQUAT 100", "MERQUAT 550", and "MERQUAT S" by the CALGON company, the quaternary polymers of vinyl pyrrolidone and vinyl imidazole, and mixtures of them.

The silicones suitable for use according to the invention are in particular the polyorganosiloxanes that are insoluble in the composition, and may be present in the form of oils, waxes, resins, or gums.

The organopolysiloxanes are defined in greater detail in the work by Water NOLL, "Chemistry and Technology of Silicones" (1968), Academie Press. They may be volatile or non-volatile.

When they are volatile, the silicones are more specifically chosen from among those with a boiling point of between 60°C and 260°C, and even more specifically among:

(I) cyclic silicones containing 3 to 7 atoms of silicon, preferably 4 to 5. They include, for example, octamethyl cyclotetrasiloxane marketed in particular under the name of "VOLATILE SILICONE 7207" by the UNION CARBIDE, or "SILBIONE 70045 V 2" by RHÔNE-POULENC, decamethyl cyclopentasiloxane marketed under the name "VOLATILE SILICONE 7158" by UNION CARBIDE, and "SILBIONE 70045 V 5" by RHÔNE-POULENC, as well as mixtures of them.

It is also worth mentioning the cyclocopolymers of the dimethyl siloxanes/methyl alkyl siloxanes type, such as "SILICONE VOLATILE FZ 3109" marketed by the UNION CARBIDE CORPORATION, the chemical structure of which is:

It is also worth mentioning blends of cyclic silicones with organic compounds derived from silicon, such as the (50/50) blend of octamethyl cyclotetrasiloxane and tetratrimethyl silyl pentaerythritol, and the blend of octamethyl cyclotetrasiloxane and oxy-1,1'(hexa-2,2,2',2'3,3'-trimethyl silyloxy) bis-neopentane;

(ii) linear volatile silicones having 2 to 9 silicon atoms and a viscosity that is less than or equal to 5•10<sup>-6</sup>m<sup>2</sup>/s at 25°C. This is, for example, decamethyl tetrasiloxane marketed in particular under the name "SH 200" by the firm TORAY SILICONE. Silicones of this category are also described in the article published in Cosmetics and Toiletries, Vol. 91, Jan. 76, pages 27-32 - TODD & BYERS "Volatile Silicone fluids for cosmetics."

It is preferable to use non-volatile silicones, and more specifically the polyalkyl siloxanes, polyaryl siloxanes, polyalkyl aryl siloxanes, silicone gums and resins, and polyorgano siloxanes modified by organofunctional groups, as well as mixtures of them.

These silicones are chosen more specifically from among the polyalkyl siloxanes, of which we can cite primarily the polydimethyl siloxanes with terminal trimethyl silyl groups having a viscosity of 5•10<sup>-6</sup> at 2.5 m<sup>2</sup>/s at 25°C, preferably of 1•10<sup>-5</sup> to 1 m<sup>2</sup>/s. The viscosity of silicone is, for example, measured at 25°C according to standard ASTM 445 Appendix C.

Among the polyalkyl siloxanes, it is possible to cite in a non-limiting way the following commercial products:

- the SILBIONE oils of the series 47 and 70 047, or the MIRASIL oils marketed by RHÔNE-POULENC, such as the oil 70 047 V 500,000;
  - the MIRASIL series of oils marketed by the RHÔNE-POULENC corporation;
- the 200 series of oils of the DOW CORNING company, such as DC200, in particular, with a viscosity of 60,000 Cst;
- the VISCASIL oils of GENERAL ELECTRIC and certain oils of the SF series (SF 96, SF 18) of GENERAL ELECTRIC.

We can also mention the polydimethyl siloxanes with terminal groups of dimethyl silanol (Dimethiconol according to the CTFA name), such as the 48 series of oils of the RHÔNE-

## POULENC corporation.

In this category of polyalkyl siloxanes, it is also worth mentioning the products marketed under the names "ABIL WAX 9800 and 9801" by the GOLDSCHMIDT company, which are polyalkyl ( $C_1$  -  $C_{20}$ ) siloxanes.

The polyalkyl aryl siloxanes are particularly chosen from among the polydimethyl methyl phenyl siloxanes and the polydimethyl diphenyl siloxanes, whether linear or branched, and with a viscosity of  $1.10^{-5}$  to  $5.10^{-2}$  m<sup>2</sup>/s at 25° C.

Among the polyalkyl aryl siloxanes, we can mention, by way of example, the products marketed under the following names:

- the SILBIONE oils of the series 70,641 of RHÔNE-POULENC;
- the RHODORSIL oils of the series 70 633 and 763 of RHÔNE-POULENC;
- the DOW CORNING 556 COSMETIC GRADE FLUID oil of DOWN CORNING;
- silicones of the PK series of BAYER, such as the PK20 product;
- silicones of the PN and PH series of BAYER, such as the products PN1000 and PH1000;
- certain oils of the SF series of GENERAL ELECTRIC, such as SF 1023, SF 1154, SF 1250, and SF 1265.

The silicone gums suitable for use according to the invention are, in particular the polydiorganosiloxanes with a high number-average molecular weight comprised between 200,000 and 1,000,000, used alone or mixed with a solvent. The solvent may be chosen from among volatile silicones, polydimethyl siloxane oils (PDMS), poly-phenyl methyl siloxane oils (PPMS), isoparaffins, polyisobutylenes, methylene chloride, pentane, dodecane, tridecane, or mixtures of them.

In particular, it is worth mentioning the following products:

- polymethyl siloxane,
- polydimethyl siloxane/methyl vinýl siloxane gums,
- polydimethyl siloxane/diphenyl siloxane,
- polydimethyl siloxane/phenyl methyl siloxane,
- polydimethyl siloxane/diphenyl siloxane/methyl vinyl siloxane.

The products particularly suitable for use according to the invention are mixtures such as:

- mixtures formed using a polydimethyl siloxane hydroxylated at the end of the chain (called dimethiconol according to the nomenclature of the CTFA dictionary) and a cyclic polydimethyl siloxane (called cyclomethicone according to the nomenclature of the CTFA dictionary), such as the product Q2 1401 marketed by the DOW CORNING company;
- mixtures formed using a polydimethyl siloxane gum with a cyclic silicone such as the product SF 1214 Silicone Fluid of GENERAL ELECTRIC; this product is an SF 30 gum corresponding to dimethicone with an average numerical molecular weight of 500,000 solubilized in SF 1202 Silicone Fluid oil, which corresponds to decamethyl cyclopentasiloxane;
- blends of two PDMS with different viscosities, and more specifically a PDMS gum with a PDMS oil, such as the products SF 1236 of GENERAL ELECTRIC. The product SF 1236 is a mixture of an SE 30 gum as defined above with a viscosity of 20 m<sup>2</sup>/s and an SF 96 oil with a viscosity of 5•10<sup>-6</sup> m<sup>2</sup>/s. This product preferably includes 15% SE 30 gum and 85% SF 96 oil.

The organopolysiloxane resins suitable for use according to the invention are reticulated siloxanic systems containing the units:

R<sub>2</sub>SiO<sub>2/2</sub>, R<sub>3</sub>SiO<sub>1/2</sub>, RSiO<sub>3/2</sub>, and SiO<sub>4/2</sub>, in which R represents a hydrocarbon group having 1 to 16 carbon atoms or a phenyl group. Among these products, the particularly preferred ones are those in which R designates a lower alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>, more specifically

methyl or a phenyl radical.

Among resins, the ones worth mentioning are the product marketed under the name "DOW CORNING 593" or those marketed under the names "SILICONE FLUID SS 4230 and SS 4267" by the GENERAL ELECTRIC firm, which are silicones with a dimethyl/trimethyl siloxane structure.

It is also worth mentioning the resins of the trimethyl siloxysilicate type marketed particularly under the names X22-4914, X21-5034, and X21-5037 by the SHIN-ETSU firm.

The organo-modified silicones suitable for use according to the invention are silicones such as those previously defined and consisting of in their structure one or more organofunctional groups attached by means of a hydrocarbon radical.

Among the organo-modified silicones, we can mention the polyorgano siloxanes consisting of:

- polyethyleneoxy and/or polypropyleneoxy groups, possibly consisting of alkyl groups composed of C<sub>6</sub>-C<sub>24</sub> such as the products known as dimethicone copolyol marketed by the DOW CORNING company under the name DC 1248, or the SILWET L 722, L7500, L 77, and L 711 oils of UNION CARBIDE, and alkyl (C<sub>12</sub>) methicone copolyol marketed by DOW CORNING under the name of Q2 5200;
- amine groups, whether substituted or not, such as the products marketed under the name GP 4 Silicone Fluid and GP 7100 by the GENESEE corporation, or the products marketed under the names Q2 8220 and DOW CORNING 929 or 939 by DOW CORNING. The substituted amine groups are preferably amino alkyl groups composed of C<sub>1</sub>-C<sub>4</sub>;
- thiol groups such as the products marketed under the names "GP 72 A" and "GP 71" by GENESEE;

- alKoxyl groups such as the products marketed under the name "SILICONE
   COPOLYMER F-755" by SWS SILICONES and ABIL WAX 2428, 2434, and 2440 by the
   GOLDSCHMIDT firm;
- hydroxylated groups such as polyorgano siloxanes with a hydroxy alkyl function as described in French Patent pending FR-A-85 16334, which corresponds to formula (XIV):

where the R<sub>3</sub> radicals, whether identical or different, are chosen from among the methyl and phenyl radicals; with at least 60 mol% of the R<sub>3</sub> radicals designating methyl; the radical R'<sub>3</sub> is a hydrocarbon divalent alkylene link composed of C<sub>2</sub>-C<sub>18</sub>; p is between 1 through 30; and q is between 1 through 150;

- acyloxy alkyl groups such as the polyorgano siloxanes described in Patent US-A-4957732 and corresponding to formula (XV):

$$R_{4} - Si - O - Si - O - Si - R_{4}$$

$$R_{4} - Si - O - Si - R_{4}$$

$$R_{4} - Si - O - Si - R_{4}$$

$$R_{5} - O - Si - R_{4}$$

$$R_{7} - O - Si - R_{4}$$

$$R_{8} - O - Si - R_{4}$$

$$R_{1} - O - Si - R_{4}$$

$$R_{2} - O - Si - R_{4}$$

$$R_{3} - O - Si - R_{4}$$

$$R_{4} - O - Si - R_{4}$$

$$R_{5} - O - Si - R_{4}$$

$$R_{5} - O - Si - R_{4}$$

$$R_{5} - O - Si - R_{5}$$

$$R_{5} - O - Si - CO$$

$$R_{5} - O - Si$$

$$R_{5} -$$

where:

R<sub>4</sub> designates a methyl, phenyl, -OCOR<sub>5</sub>, or hydroxyl group, while only one radical R<sub>4</sub> per atom of silicon can be OH;

R'4 designates methyl, phenyl; with at least 60% in molar proportion of the set of R4 and

R'4 radicals designating methyl;

R<sub>5</sub> designates alkyl or alkenyl composed of C<sub>8</sub>-C<sub>20</sub>;

R" designates a linear or branched divalent hydrocarbon alkylene radical composed of  $C_2$ - $C_{18}$ ;

r is between 1 through 120;

p is between 1 and 30;

q is equal to 0 or is less than 0.5 p, with p + q being between 1 and 30; the polyorganosiloxanes of formula (XV) may contain the following groups:

in proportions that do not exceed 15% of the sum of p + q + r.

- anionic groups of the carboxylic type, such as in the products described in Patent EP 186 507 of the CHISSO CORPORATION, or of the alkyl carboxylic type such as those present in the product X-22-3701E of the SHIN-ETSU company; 2-hydroxy alkyl sulfonate; 2-hydroxy alkyl thiosulfonate such as the products marketed by the GOLDSCHMIDT company under the names "ABIL S201" and "ABIL S255".

- hydroxy acylamino groups, such as the polyorgano siloxanes described in Patent pending EP 342 834. The product Q2-8413 of the DOW CORNING company, for example, is worth mentioning.

According to the invention, it is also possible to use silicones consisting of a portion of polysiloxane and a portion consisting of a non-siliconated organic chain, one of the two portions constituting the main chain of the polymer and the other being grafted to said main chain. These polymers are, for example, described in Patents pending EP-A-412 704, EP-A-412 707, EP-A-

640 105, and WO 95/00578, EP-A-582 152 and WO 93/23009, and Patents US 4,693,935, US 4,728,571, and US 4,972,037. These polymers are preferably anionic or non-ionic.

These polymers are, for example, copolymers which may be obtained by radicular polymerization from a blend of monomers consisting of:

- a) 50 to 90% by weight of tertiobutyl acrylate;
- b) 0 to 40% by weight of acrylic acid;
- c) 5 to 40% by weight of a siliconated macromer of the formula:

$$H_{2}C = C - C - O - (CH_{2})_{3} - SI - O - (CH_{3})_{3} - SI - O - (CH_{3})_{3} - CH_{3} - CH_{3}$$

with v being a number from 5 to 700; the percentages by weight being calculated in relation to the total weight of the monomers.

Other examples of grafted siliconated polymers are, in particular, the polydimethyl siloxanes (PDMS) to which are grafted, by means of a thiopropylene type of connecting link, mixed polymer units of the poly(meth)acrylic acid type and of the alkyl poly(meth)acrylate type, and the polydimethyl siloxanes (PDMS) to which are grafted, by means of a thiopropylene type of connecting link, polymer units of the isobutyl poly(meth)acrylate type.

According to the invention, all the silicones may also be used in the form of emulsions, nano-emulsions, or micro-emulsions.

The polyorgano siloxanes that are particularly preferred according to the invention are:

- the non-volatile silicones chosen from the family of polyalkyl siloxanes with trimethyl silyl terminal groups, such as oils having a viscosity comprised between 0.2 and 2.5 m<sup>2</sup>/s at 25° C, such as the oils from the DC200 series of DOW CORNING, in particular the one with a

viscosity of 60,000 Cst, the SILBIONE 70047 and 47 series, and in particular the oil 70 047 V 500 000 marketed by the RHÔNE-POULENC company, the polyalkyl siloxanes with dimethyl silanol terminal groups such as dimethical, or the polyalkyl aryl siloxanes such as the oil SILBIONE 74061 V 200 marketed by RHÔNE-POULENC;

- the organopolysiloxane resin marketed under the name DOW CORNING 593;
- the polysiloxanes with amine groups such as amidomethicone or the trimethyl silyl amidomethicone;

The proteins or hydrolyzed cationic proteins are, in particular, chemically modified polypeptides carrying at the end of the chain, or grafted to it, quaternary ammonium groups. Their molecular weight may vary, for example, from 1,500 to 10,000, and in particular from about 2,000 to 5,000.

Among these compounds, we can mention in particular:

- hydrolyzed collagens carrying triethyl ammonium groups such as the products sold under the name "Quat-Pro E" by the MAYBROOK company, and referred to in the CTFA dictionary as "Triethonium Hydrolyzed Collagen Ethosulfate";
- hydrolyzed collagens carrying groups of trimethyl ammonium and trimethyl stearyl ammonium chloride, sold under the name "Quat-Pro S" by the MAYBROOK company and referred to in the CTFA dictionary as "Steartrimonium Hydrolyzed Collagen";
- hydrolyzed animal proteins carrying trimethyl benzyl ammonium groups such as the products sold under the name "Crotein BTA" by the CRODA firm, and referred to in the CFTA dictionary as "Benzyltrimonium hydrolyzed animal protein";
- hydrolyzed proteins carrying groups of quaternary ammonium on the polypeptide chain, including at least one alkyl radical having 1 to 18 atoms of carbon.

Among the hydrolyzed proteins, it is worth mentioning, among others:

- "Croquat L" in which the quaternary ammonium groups include an alkyl group composed of C<sub>12</sub>;
- "Croquat M" in which the quaternary ammonium groups include alkyl groups composed of  $C_{10}$ - $C_{18}$ ;
- "Croquat S" in which the quaternary ammonium groups include an alkyl group composed of  $C_{18}$ ;
- "Crotein Q" in which the quaternary ammonium groups include at least one alkyl group having from 1 to 18 atoms of carbon.

These various products are sold by the Croda company.

Other proteins or quaternized hydrolyzates are, for example, those corresponding to the formula:

$$\begin{array}{c} \text{CH}_3 \\ \downarrow \\ \parallel \\ \parallel \\ \parallel \\ \text{CH}_3 \end{array} - \text{NH-A} \qquad \text{XO} \qquad \text{(XVII)}$$

where X is an anion of an organic or mineral acid, A designates a protein remnant derived from hydrolyzed collagen protein, R<sub>5</sub> designates a lipophilic group containing up to 30 carbon atoms, R<sub>6</sub> represents an alkylene group having 1 to 6 carbon atoms. It is possible to mention, for example, the products sold by the Inolex company, under the name "Lexein QX 3000", which is referred to in the CTF dictionary as "Cocotrimonium Collagent Hydrolysate."

In addition, we can mention quaternized vegetable proteins such as wheat, corn, or soy proteins: by way of quaternized wheat proteins we can cite those marketed by the Croda company under the names "Hydrotriticum WQ or QM" and referred to in the CTFA dictionary

as "Cocodimonium Hydrolyzed wheat protein," "Hydrotriticum QL" referred to in the CTFA dictionary as "Laurdimonium hydrolysed wheat protein," or further, "Hydrotriticum QS", known in the CTFA dictionary as "Steardimonium hydrolysed wheat protein."

According to the invention, ceramide types of compounds are in particular the ceramides and/or glycoceramides and/or pseudoceramides and/or neoceramides, whether natural or synthetic.

Compounds of the ceramide type are, for example, described in Patents pending DE4424530, DE4424533, DE4402929, DE4420736, WO95/23807, WO94/07844, EP-A-0646572, WO95/16665, FR-2 673 179, EP-A-0227994, WO 94/07844, WO 94/24097, and WO 94/10131, the information from which is included herein by way of reference.

The ceramide type compounds particularly preferred according to the invention are, for example:

- 2-N-linoleoyl amino-octadecane-1,3-diol,
- 2-N-oleoyl amino-octadecane-1,3-diol,
- 2-N-palmitoyl amino-octadecane-1,3-diol,
- 2-N-stearoyl amino-octadecane-1,3-diol,
- 2-N-behenoyl amino-octadecane-1,3-diol,
- 2-N-[2-hydroxy-palmitoyl]-amino-octadecane-1,3-diol,
- 2-N-stearoyl amino-octadecane-1,3,4-triol and in particular N-stearoyl phytosphingosine,
  - 2-N-palmitoyl amino-hexadecane-1,3-diol,
  - (bis-(N-hydroxy ethyl N-cetyl) malonamide),
  - N(2-hydroxy ethyl)-N-(3-cetoxyl-2-hydroxy propyl) amide of cetylic acid,

- N-docosanoyl N-methyl-D-glucamine, or mixtures of such compounds.

It is also possible to use cationic surfactants, among which we can mention, in particular: salts of primary, secondary, or tertiary fatty amines, possibly polyoxyalkylenated; quaternary ammonium salts; derivatives of imadazoline; or amine oxides that are cationic in nature.

The quaternary ammonium salts are, for example:

- those having the following general formula (XVIII):

$$\begin{bmatrix} R_1 & R_3 \\ R_2 & R_4 \end{bmatrix}^+ X^-$$
(XVIII)

where the radicals R<sub>1</sub> to R<sub>4</sub>, which may be identical or different, represent an aliphatic radical, whether linear or branched, consisting of 1 to 30 atoms of carbon, or an aromatic radical such as an aryl or an alkyl aryl. The aliphatic radical may include heteroatoms such as, in particular, oxygen, nitrogen, sulfur, or halogens. The aliphatic radicals are, for example, chosen from among the alkyl, alkoxy, polyoxyalkylene(C<sub>2</sub>-C<sub>5</sub>), alkylamide, alkyl(C<sub>12</sub>-C<sub>22</sub>)amido alkyl(C<sub>2</sub>-C<sub>6</sub>), alkyl(C<sub>12</sub>-C<sub>22</sub>)acetate, and hydroxy alkyl radicals, consisting of about 1 to 30 carbon atoms; X is an anion chosen from among the group of halogenides, phosphates, acetates, lactates, alkyl(C<sub>2</sub>-C<sub>6</sub>)sulfates, alkyl- or alkyl aryl sulfonates,

- quaternary ammonium salts of imidazolinium, such as in the following formula (XIX):

$$\begin{bmatrix} R_8 & CH_2-CH_2-N(R_8)-CO-R_8 \\ N & R_7 \end{bmatrix}^+ X^-$$
(XIX)

where R<sub>5</sub> represents an alkenyl or alkyl radical including 8 to 30 carbon atoms derived, for

example, from tallow fatty acids, R<sub>6</sub> represents an atom of hydrogen, an alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>, or an alkenyl or alkyl radical containing 8 to 30 atoms of carbon, R<sub>7</sub> represents an alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>, R<sub>8</sub> represents a hydrogen atom, an alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>, X is an anion chosen from among the group of halogenides, phosphates, acetates, lactates, alkyl sulfates, or alkyl- or alkyl aryl sulfonates. R<sub>5</sub> and R<sub>6</sub> preferably designate a mixture of an alkenyl or alkyl radicals consisting of from 12 to 21 carbon atoms, derived for example from tallow fatty acids, R<sub>7</sub> designates methyl, and R<sub>8</sub> designates hydrogen. Such a product is, for example, marketed under the name "REWOQUAT W 75" by the REWO corporation.

- quaternary ammonium salts of the formula (XX):

$$\begin{bmatrix} R_{10} & R_{12} \\ I & I^{12} \\ R_{9} - N - (CH_{2})_{3} & N - R_{14} \\ R_{11} & R_{13} \end{bmatrix} + + 2X$$
(XX)

where R<sub>9</sub> represents an aliphatic radical consisting of about 16 to 30 carbon atoms, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, and R<sub>14</sub>, whether identical or different, are selected from between hydrogen and an alkyl radical consisting of from 1 to 4 carbon atoms, and X is an anion chosen from the group of halogenides, acetates, phosphates, nitrates, and methyl sulfates. Such quaternary salts of diammonium include, in particular, tallow propane diammonium dichloride.

- quaternary ammonium salts containing at least one ester function.

The quaternary ammonium salts containing at least one ester function that are suitable for use according to the invention are, for example, those having the following formula (XXI):

$$\begin{array}{c|c}
C_{1} & C_{1} & C_{2} & C_{1} \\
R_{17} & C & C_{2} & C_{2} \\
R_{15} & C & C_{2} & C_{2} \\
\end{array}$$

$$\begin{array}{c|c}
C_{1} & C_{2} & C_{2} & C_{2} \\
C_{2} & C_{2} & C_{2} \\
C_{3} & C_{4} & C_{4} \\
C_{4} & C_{5} & C_{4} \\
C_{5} & C_{5} & C_{4} \\
C_{5} & C_{5} & C_{4} \\
C_{5} & C_{5} & C_{5} \\
C_{5}$$

where:

- $R_{15}$  is chosen from among alkyl radical composed of  $C_1$ - $C_6$ , and the hydroxy alkyl or dihydroxy alkyl radicals composed of  $C_1$ - $C_6$ ;
  - R<sub>16</sub> is chosen from among:
  - the radical  $R_{\overline{B}}$  C-
- the hydrocarbon  $R_{20}$  radicals composed of  $C_1$ - $C_{22}$ , whether linear or branched, saturated or unsaturated,
  - a hydrogen atom,
  - R<sub>18</sub> is chosen from among:
  - R<sub>zi</sub>C-
- the hydrocarbon R<sub>22</sub> radicals composed of C<sub>1</sub>-C<sub>6</sub>, whether linear or branched, saturated or unsaturated,
  - a hydrogen atom,

 $R_{17}$ ,  $R_{19}$ , and  $R_{21}$ , whether identical or different, are selected from among hydrocarbon radicals composed of  $C_7$ - $C_{21}$ , whether linear or branched, saturated or unsaturated;

- -n, p, and r, whether identical or different, are whole numbers from 2 to 6;
- y is a whole number from 1 to 10;
- x and z, whether identical or different, are whole numbers from 0 to 10;

- X- is a simple or complex, organic or inorganic anion; provided that the sum of x + y + z equals 1 to 15, that when x equals 0, then  $R_{16}$  designates  $R_{20}$ , and when z equal 0 then  $R_{18}$  designates  $R_{22}$ .

The R<sub>15</sub> alkyl radicals may be linear or branched, but preferably linear.

R<sub>15</sub> preferably designates a methyl, ethyl, hydroxy ethyl, or dihydroxy ethyl radical, and more specifically a methyl or ethyl radical.

The sum of x + y + z is advantageously from 1 to 10.

When  $R_{16}$  is a hydrocarbon  $R_{20}$  radical, it may be long and have 12 to 22 atoms of carbon, or short and have 1 to 3 atoms of carbon.

When R<sub>18</sub> is a hydrocarbon R<sub>22</sub> radical, it preferably has 1 to 3 atoms of carbon.

 $R_{17}$ ,  $R_{19}$ , and  $R_{21}$ , whether identical or different, are advantageously chosen from among hydrocarbon radicals composed of  $C_{11}$  to  $C_{21}$ , whether linear or branched, saturated or unsaturated, and more specifically among the alkyl and alkenyl radicals composed of  $C_{11}$  to  $C_{21}$ , linear or branched, saturated or unsaturated.

Preferably, x and z, whether identical or different, equal 0 or 1.

Advantageously, y is equal to 1.

Preferentially, n, p, and r, whether identical or different, equal 2 or 3, and even more specifically, they are equal to 2.

The anion is preferably a halogenide (chloride, bromide, or iodide) or an alkyl sulfate, and more specifically a methyl sulfate. However, it is possible to use methane sulfonate, phosphate, nitrate, tosylate, an anion derived from an organic acid such as acetate or lactate, or any other anion that is compatible with an ester function ammonium.

The anion X- is even more specifically chloride or methyl sulfate.

The ammonium salts from formula (XXI) that are more particularly used are those in which:

- R<sub>15</sub> designates a methyl or ethyl radical;
- x and y are equal to 1;
- z is equal to 0 or 1;
- n, p, and r are equal to 2;
- R<sub>16</sub> is chosen from among:

- the radical 
$$R_{\overline{19}}$$
  $C-$ 

- the methyl, ethyl, or hydrocarbon radicals composed of  $C_{14}$  to  $C_{22}$ ,
- an atom of hydrogen;
- R<sub>18</sub> is chosen from among:

- an atom of hydrogen;

 $R_{17}$ ,  $R_{19}$ , and  $R_{21}$ , whether identical or different, are chosen from among hydrocarbon radicals composed of  $C_{13}$  to  $C_{17}$ , whether linear or branched, saturated or unsaturated, and preferably from among the alkyl and alkenyl radicals composed of  $C_{13}$  to  $C_{17}$ , whether linear or branched, saturated or unsaturated.

The hydrocarbon radicals are advantageously linear.

We can cite, for example, compounds from formula (XXI) such as salts (particularly chloride or methyl sulfate) of diacyloxy ethyl dimethyl ammonium, diacyloxy ethyl hydroxy

ethyl methyl ammonium, monoacyloxy ethyl dihydroxy ethyl methyl ammonium, triacyloxy ethyl methyl ammonium, monoacyloxy ethyl hydroxy ethyl dimethyl ammonium and mixtures of them. The alkyl radicals preferably have 14 to 18 carbon atoms and originate more specifically from a vegetable oil such as palm oil or sunflower oil. When the compound has several alkyl radicals they may be identical or different.

These products are obtained, for example, by direct esterification of triethanolamine, triisopropanolamine, alkyl diethanolamine, or alkyl di-isopropanolamine, possibly oxyalkylenated
with fatty acids or blends of fatty acids of vegetable or animal origin, or by transesterifying their
methylic esters. This esterification is followed by quaternization using an alkalinizing agent
such as an alkyl (preferably methyl or ethyl) halogenide, a dialkyl (preferably methyl or ethyl)
sulfate, methyl methane sulfonate, methyl paratoluene sulfonate, chlorhydrine of glycol or
glycerol.

These compounds are, for example, marketed under the names DEHYQUART by the HENKEL company, STEPANQUAT by the STEPAN company, NOXAMIUM by the CECA firm, and REWOQUAT WE 18 by the REWOWITCO company.

It is also possible to use ammonium salts containing at least one ester function as described in Patents US-A-4874554 and US-A-4137180.

Among the quaternary ammonium salts of formula (XVIII), the preferred ones are, on the one hand, tetra alkyl ammonium chlorides, such as the dialkyl dimethyl ammonium or alkyl trimethyl ammonium chlorides, in which the alkyl radical contains about 12 to 22 carbon atoms, particularly the behenyl trimethyl ammonium, distearyl dimethyl ammonium, cetyl trimethyl ammonium, benzyl dimethyl stearyl ammonium chlorides, or even, on the other hand, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride marketed under the name

"CERAPYHL 70" by the VAN DYK corporation.

The fatty acids are chosen more particularly from among myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid, and isostearic acid.

The derivatives of fatty acids are specifically the carboxylic ester acids, in particular the mono, di, tri, or tetra carboxylic esters.

The monocarboxylic esters are specifically the monoesters of saturated or unsaturated, linear or branched aliphatic acids composed of  $C_1$  to  $C_{26}$ , and saturated or unsaturated, linear or branched aliphatic alcohols composed of  $C_1$  to  $C_{26}$ , the total carbon number of these esters being greater than or equal to 10.

Among the monoesters, we can mention dihydroabietyl behenate; octyl dodecyl behenate; isocetyl behenate, cetyl lactate, alkyl lactate composed of C<sub>12</sub> to C<sub>15</sub>, isostearyl lactate; lauryl lactate; linoleyl lactate; oleyl lactate; (iso)stearyl octanoate; isocetyl octanoate; octyl octanoate; decyl oleate; isocetyl isostearate; isocetyl laurate; isocetyl stearate; isodecyl octanoate; isodecyl oleate; isononyl isononanoate; isostearyl palmitate; methyl acetyl ricinoleate; myristyl stearate; octyl isononanoate; 2-ethyl hexyl isononate; octyl palmitate; octyl pelargonate; octyl stearate; octyl dodecyl erucate; oleyl erucate; the ethyl and isopropyl palmitates, ethyl-2-hexyl palmitate; 2-octyl decyl palmitate; alkyl myristates such as isopropyl, butyl, cetyl, and 2-octyl dodecyl myristate; hexyl stearate, butyl stearate, isobutyl stearate; dioctyl malate, hexyl laurate, 2-hexy decyl laurate.

It is also possible to use esters of di- or tricarboxylic acids with  $C_4$  to  $C_{22}$  and esters of mono-di- or tricarboxylic acids, and of di-, tri-, tetra-, or pentahydroxy alcohols with  $C_2$  to  $C_{26}$ .

In particular we can mention: diethyl sebacate; di-isopropyl sebacate; di-isopropyl adipate; di-n-propyl adipate; di-octyl adipate; di-isostearyl adipate; di-octyl maleate; glyceryl

undecylenate; octyl dodecyl stearoyl stearate; pentaerythrityl monoricinoleate; pentaerythrityl tetraisononanoate; pentaerythrityl tetrapelargonate; pentaerythrityl tetraisostearate; pentaerythrityl tetraoctanoate; dicaprylate; propylene glycol dicaprate; tridecyl erucate; triisopropyl citrate; tri-isostearyl citrate; glyceryl trilactate; glyceryl trioctanoate; trioctyl dodecyl citrate; trioleyl citrate.

Among the abovementioned esters, it is preferable to use the ethyl and isopropyl palmitates, ethyl-2-hexyl palmitate; 2-octyl decyl palmitate; the alkyl myristates such as isopropyl, butyl, cetyl, and 2-octyl dodecyl myristate; hexyl stearate, butyl stearate, isobutyl stearate, dioctyl malate, hexyl laurate, 2-hexyl decyl laurate, isononyl isononanate, and cetyl octanoate.

The fluoridated oils are, for example, the perfluoropolyethers described in particular in Patent pending EP-A-486135, and the fluorohydrocarbon compounds described in particular in Patent pending WO 93/11103. The discoveries contained in those two Patents are entirely included within this Patent application by way of reference.

The term fluorohydrocarbon compounds refers to compounds the chemical structure of which includes a carbonaceous skeleton in which some hydrogen atoms have been substituted by fluorine atoms.

The fluoridated oils may also be fluorocarbons such as fluoramines, perfluorotributylamine, for example, fluoridated hydrocarbons, such as perfluorodecahydronaphthalene, fluoroesters, and fluoroethers;

Perfluoropolyethers are, for example, sold under the brand names FOMBLIN by the MONTEFLUOS company and KRYTOX by the DU PONT company.

Among the fluorohydrocarbon compounds, it is also worth mentioning the esters of

fluoridated fatty acids such as the products sold under the name NOFABLE FO by the NIPPON OIL corporation.

Naturally, it is possible to use blends of conditioning agents.

According to the invention, the conditioning agent or agents may represent from 0.001% to 20% by weight, and preferably from 0.01% to 10% by weight, and even more specifically from 0.1% to 3% by weight in relation to the total weight of the final composition.

In addition, the compositions according to the invention advantageously include at least one surfactant, which is generally present in an amount comprised between about 0.1% and 60% by weight, preferably between 1% and 40%, and even more preferentially between 5% and 30%, in relation to the total weight of the composition.

This surfactant may be chosen from among anionic, amphoteric, or non-ionic surfactants, or mixtures of them.

The surfactants suitable for use in the invention are the following in particular:

# (I) Anionic Surfactant(s):

By their very nature, they are not truly critical within the context of the invention.

So, by way of example, the surfactants suitable for use, whether alone or blended, within the context of the invention include in particular (non-limiting list) the salts (particularly alkaline salts, specifically sodium, ammonium salts, amine salts, amino-alcohol salts, magnesium salts) of the following compounds: alkyl sulfates, alkyl ether sulfates; alkyl amidoether sulfates, alkyl aryl polyether sulfates; monoglyceride sulfates; alkyl sulfonates; alkyl phosphates; alkylamide sulfonates; alkyl aryl sulfonates; α-olefin-sulfonates; paraffin-sulfonates; alkyl sulfosuccinates; alkyl ether sulfosuccinates; alkylamide sulfosuccinates; alkyl sulfosuccinamates; alky

the alkyl or acyl radical of all these various compounds preferably containing 8 to 24 carbon atoms, and the aryl radical preferably designating a phenyl or benzyl group. Among further anionic surfactants suitable for use, we can mention the salts of fatty acids such as salts of oleic, ricinoleic, palmitic, and stearic acids, copra oil or hydrogenated copra oil acids; and the acyl lactylates in which the acyl radical contains 8 to 20 carbon atoms. It is also possible to use slightly anionic surfactants, such as the uronic D galactoside alkyl acids and their salts, as well as the polyoxyalkylene carboxylic alkyl (C<sub>6</sub> to C<sub>24</sub>) ether acids, polyoxyalkylenated carboxylic alkyl (C<sub>6</sub> to C<sub>24</sub>) aryl ether acids, polyoxyalkylenated carboxylic alkyl (C<sub>6</sub> to C<sub>24</sub>) amido ether acids and their salts, in particular those consisting of from 20 to 50 groups of ethylene oxide, and mixtures of them

Among the anionic surfactants according to the invention, it is preferable to use the salts of alkyl sulfates and alkyl ether sulfates, and mixtures of them.

# (ii) Non-ionic Surfactant(s):

The non-ionic surfactants are also well-known compounds (in this regard, see "Handbook of Surfactants" by M.R. PORTER, Blackie & Son editions (Glasgow and London), 1991, pages 116-178), and within the context of the invention, their nature is not critical. So, in particular they may be chosen from among (non-limiting list) alcohols, alpha-diols, alkyl phenols, or polyethoxylated, polypropoxylated, or polyglycerolated fatty acids, having a fatty chain containing, for example, from 8 to 18 carbon atoms, the number of ethylene oxide or propylene oxide groups ranging specifically from 2 to 50, and the number of glycerol groups ranging from 2 to 30. We can also mention the ethylene and propylene oxide polymers, condensates of ethylene and propylene oxide in fatty alcohols; polyethoxylated fatty amides preferably having from 2 to 30 mole of ethylene oxide, polyglycerolated fatty amides consisting of on average 1 to

5 groups of glycerol, and in particular 1.5 to 4; polyethoxylated fatty amides preferably having 2 to 30 mole ethylene oxide; fatty acid esters of oxyethylenated sorbitan having 2 to 30 mole ethylene oxide; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkyl polyglycosides, derivatives of N-alkyl glucamine, amine oxides such as alkyl (C<sub>10</sub> to C<sub>14</sub>) amine oxides, or N-acyl amino propyl morpholine oxides. It should be noted that the alkyl polyglycosides are non-ionic surfactants that work particularly well within the context of the invention.

### (iii) Amphoteric Surfactants:

Amphoteric surfactants, the nature of which is not critical within the context of the invention, may include, in particular (non-limiting list) derivatives of aliphatic secondary or tertiary amines, in which the aliphatic radical is a linear or branched chain consisting of 8 to 22 carbon atoms and containing at least one hydrosolubilizing anionic group (for example, carboxylate, sulfonate, sulfate, phosphate, or phosphonate); we can also mention the alkyl (C<sub>8</sub> to C<sub>20</sub>) betaines, sulfobetaines, alkyl (C<sub>8</sub> to C<sub>20</sub>) amidoalkyl (C<sub>1</sub> to C<sub>6</sub>) betaines, or the alkyl (C<sub>8</sub> to C<sub>20</sub>) amidoalkyl (C<sub>1</sub> to C<sub>6</sub>) sulfobetaines.

Among the amine derivatives, we can mention the products marketed under the name MIRANOL, such as the ones described in Patents US-2,528,378 and US-2,781,354, and with structures:

 $R_2$ -CONHCH<sub>2</sub>CH<sub>2</sub> - N( $R_3$ )( $R_4$ )(CH<sub>2</sub>COO-) (2)

where: R<sub>2</sub> designates an alkyl radical derived from an R<sub>2</sub>-COOH acid present in hydrolyzed copra oil, a heptyl, nonyl, or undecyl radical, R<sub>3</sub> designates a beta-hydroxy ethyl group, and R<sub>4</sub> a carboxymethyl group;

and

$$R_2$$
-CONHCH<sub>2</sub>CH<sub>2</sub> - N(B)(C) (3)

where:

B represents to  $CH_2CH_2OX$ , C represents -( $CH_2$ )<sub>z</sub> -Y', with z = 1 or 2,

X' designates the group to CH<sub>2</sub>CH<sub>2</sub>COOH or an atom of hydrogen,

Y' designates to COOH or the radical to CH2 - CHOH - SO3H,

 $R_5$  designates an alkyl radical of an  $R_9$ -COOH acid present in copra oil or in hydrolyzed flax oil, an alkyl radical, particularly composed of  $C_7$ ,  $C_9$ ,  $C_{11}$ , or  $C_{13}$ , an alkyl radical composed of  $C_{17}$  and its iso- form, and an unsaturated  $C_{17}$  radical.

These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names Disodium Cocoamphodiacetate, Disodium Lauroamphodiacetate, Disodium Caprylamphodiacetate, Disodium Cocoamphordipropionate, Disodium Lauroamphodipropionate, Disodium Caprylamphodipropionate, disodium Caprylamphodipropionate, Lauroamphodipropionic acid, and Cocoamphodipropionic acid.

By way of example, we can mention cocoamphodiacetate marketed under the brand name concentrated MIRANOL C2M by the RHÔNE-POULENC company.

In compositions according to the invention, it is preferable to use blends of surfactants, and particularly blends of anionic surfactants and blends of anionic surfactants and amphoteric or non-ionic surfactants. A particularly preferred blend contains at least one anionic surfactant and at least one amphoteric surfactant.

It is preferable to use an anionic surfactant chosen from among the alkyl( $C_{12}$  to  $C_{14}$ ) sulfates of sodium, triethanolamine, or ammonium, alkyl( $C_{12}$  to  $C_{14}$ ) ether sulfates of

oxyethylenated sodium, triethanolamine, or ammonium with 2.2 mole of ethylene oxide, sodium cocoyl isethionate, and alpha olefin( $C_{14}$  to  $C_{15}$ ) sodium sulfonate and their mixtures with:

- either an amphoteric surfactant such as the amine derivatives known as disodium cocoamphodipropionate or sodium cocoamphopropionate, marketed specifically by the RHÔNE-POULENC company under the brand name "MIRANOL C2M CONC" in an aqueous solution of 38% active material, or under the name MIRANOL C32;

- or an amphoteric surfactant of the zwitterionic type, such as the alkyl betaines and specifically cocobetaine marketed under the name "DEHYTON AB 30" in an aqueous solution of 32% active material by the HENKEL company.

The composition according to the invention may also contain at least one additive chosen from among thickeners, perfumes, pearlizing agents, preservatives, anionic or non-ionic polymers, non-cationic proteins, hydrolyzed non-cationic proteins, methyl-18 eicosanoic acid, hydroxy acids, other polymers than those of the invention, and in particular the cationic or non-ionic polyether associative polyurethanes, and any other additive traditionally used in the cosmetic field that does not affect the properties of the compositions according to the invention.

These additives are present in the composition according to the invention in proportions that may range from 0 to 20% by weight in relation to the total weight of the composition. The precise amount of each additive may be easily determined by an expert in the field according to its nature and its function.

The compositions according to the invention may be more specifically used to wash and treat keratinous material such as hair, skin, eyelashes, eyebrows, fingernails, lips, hairy skin, and more specifically the hair.

In particular, compositions according to the invention are detergent compositions such as

shampoos, bath gels, and bubble baths. In this mode of embodiment of the invention, the compositions will comprise a generally aqueous washing base.

The surfactant or surfactants that form the washing base may be chosen indiscriminately, alone or in blends, from among the anionic, amphoteric, or non-ionic surfactants defined hereinabove.

The quantity and quality of the washing base shall be sufficient to impart a satisfactory foaming and/or detergent value to the final composition.

Therefore, according to the invention, the washing base may represent from 4% to 50% by weight, preferably from 6% to 35% by weight, and even more preferentially from 8% to 25% by weight of the total weight of the final composition.

The pH of the composition applied to the keratinous material is generally comprised between the values of 2 and 11. It is preferably comprised between 3 and 8, and may be adjusted to the desired value by means of acidifying or alkalinizing agents that are well-known in the state of the art in compositions applied to keratinous materials.

Among alkalinizing agents, we can mention, by way of example, ammonia, alkaline carbonates, alcanolamines such as mono-, di- and triethanolamines and their derivatives, hydroxy alkylamines and the oxyethylenated or oxypropylenated ethylene diamines, the sodium or potassium hydroxides, and compounds having the following formula (XXII):

$$R_{30} \sim N - R - N < R_{40} \sim (XXII)$$

where R is a propylene remnant, possibly substituted by a hydroxyl group or an alkyl radical composed of  $C_1$  to  $C_4$ ;  $R_{38}$ ,  $R_{39}$ ,  $R_{40}$ , and  $R_{41}$ , whether identical or different, represent an atom of hydrogen, an alkyl radical composed of  $C_1$  to  $C_4$ , or a hydroxy alkyl radical composed of  $C_1$ 

to C<sub>4</sub>.

By way of example, the acidifying agents are traditionally such mineral or organic acids as hydrochloric acid, orthophosphoric acid, carboxylic acids such as tartaric acid, citric acid or lactic acid, or the sulfonic acids.

The physiological and specifically cosmetically acceptable medium may consist exclusively of water, a cosmetically acceptable solvent, or a blend of water and a cosmetically acceptable solvent, particularly such as a lower alcohol composed of C<sub>1</sub> to C<sub>4</sub>, such as ethanol, isopropanol, tertiobutanol, n-butanol; the alkylene glycols such as propylene glycol, and the glycol ethers.

The invention also has as its object a process for treating keratinous material such as the skin or hair, characterized in that it consists of applying to the keratinous materials a cosmetic composition as described above, and then eventually rinsing it with water.

So, the process according to the invention makes it possible to maintain the hairstyle, treatment, care, washing, or make-up removal of the skin, the hair, and any other keratinous material.

The compositions according to the invention may also take the form of after-shampoo compositions, to be rinsed off or not, for permanents, straightening, dying, or bleaching, or moreover, the form of rinse compositions to be applied before or after dying, bleaching, permanents, or straightening, or even between the two stages of a permanent or straightening process.

The compositions according to the invention may also take the form of skin-washing compositions, and particularly in the form of solutions or gels for the bath or shower, or of make-up removal products.

The compositions according to the invention may also be in the form of aqueous or hydro-alcoholic solutions for skin and/or hair care.

The cosmetic compositions according to the invention may also be in the form of a gel, milk, cream, emulsion, thick lotion, or mousse, and may be used for the skin, fingernails, eyelashes, lips, and more specifically for the hair.

The compositions may be packaged in various forms, particularly in sprays, pump bottles, or in aerosol containers in order to apply the composition in the form of a spray or mousse. These types of packaging are indicated, for example, when one wishes to obtain a spray, hair spray, or mousse for treating the hair.

In all that follows and precedes, the expressed percentages are by weight. The invention will now be more thoroughly illustrated by means of the following examples, which shall not be considered in any way limited to the described modes of embodiment. In the examples, MA signifies active material.

Polymer 1 is a vinyl pyrrolidone / dimethyl amino propyl methacrylamide / lauryl dimethyl methacrylamidoammonium chloride terpolymer, offered by the ISP corporation under reference POLYMER ACP-1234.

### EXAMPLE 1

A shampoo composition is made:

- Sodium lauryl ether sulfate with 2.2 mole of ethylene oxide at 28% of MA 17 g MA

- Cocoyl betaine at 30% of MA

2.5 g MA

- Polymer 1

1 g MA

- Mono-isoproanolamide of copra acid

0.6 g MA

- 2-hydroxy 4-methoxy benzophenone sulfonic acid

(UNIVUL MS 40 of BASF)

0.1 g MA

- Perfume, preservatives

qs

- Demineralized water qsp

100 g

The hair treated with this shampoo is smooth, soft, and protected from the damaging effects of light.

# EXAMPLE 2

The following shampoo composition is made:

- Sodium lauryl ether sulfate with 2.2 mole of ethylene oxide at 30% of MA 10 g MA

- Cocoyl betaine at 30% of MA

4 g MA

- Polymer 1

0.5 g MA

- Polydimethyl siloxane with a viscosity of 300,000 cSt

(AK300000 Silicone of WACKER)

0.5 g MA

- Xanthan gum

1 g

-Citric acid qs pH

7

- Demineralized water qsp

100 g

The hair treated with this shampoo is smooth and soft.

## EXAMPLE 3

An after-shampoo product according to the invention is made with the following composition:

- Polymer 1

0.5 g MA

- Behenyl trimethyl ammonium chloride

- Mixture of stearylic cetyl alcohol and 33 OE oxyethelenated

stearylic cetyl alcohol (80/20)

4 g MA

- Demineralized waterqsp

100 g

The hair treated with this shampoo is smooth and soft.

# EXAMPLE 4

An after-shampoo product according to the invention is made with the following composition:

10	0.5 g MA
hloride	1.5 g MA
	0.5 g MA
• 7	100 g
	chloride

The hair treated with this shampoo is smooth and soft.

#### **CLAIMS**

- 1. Composition for treatment of keratinous materials, in particular human keratinous fibers such as hair, consisting of, in a physiologically and in particular cosmetically acceptable medium, at least one agent protecting and/or conditioning the keratinous materials and at least one cationic poly(alkyl) vinyllactam polymer consisting of:
- a) at least one vinyllactam or alkyl(C<sub>1</sub>-C<sub>5</sub>) vinyllactam type monomer
- b) at least one monomer chosen from among those with structures (I) and (II):

$$CH_{\overline{g}}-C(R_{1})-CO-X-(Y)_{\overline{p}}-(CH_{2}-CH_{2}-O)_{\overline{m}}-(CH_{2}-CH(R_{2})-O)_{\overline{n}}-(Y_{1})_{\overline{q}}-N-R_{4}$$
(i)  $Z^{-R_{5}}$ 

$$CH_{2}-C(R_{1})-CO-X-(Y)_{p}-(CH_{2}-CH_{2}-O)_{m}-(CH_{2}-CH(R_{2})-O)_{n}-(Y_{1})_{q}-N = R_{3}$$

where:

X designates an atom of oxygen or a radical NR<sub>6</sub>,

 $R_1$  and  $R_6$  each independently designates either an atom of hydrogen or a linear or branched alkyl radical composed of  $C_1$ - $C_5$ ,

R<sub>2</sub> designates a linear or branched alkyl radical composed of C<sub>1</sub>-C<sub>4</sub>,

 $R_3$ ,  $R_4$ , and  $R_5$  each independently designates an atom of hydrogen, a linear or branched alkyl radical composed of  $C_1$ - $C_{30}$ , or a radical from formula (III):

$$---(Y_2)_r -- (CH_2 - CH(R_7) - O)_r -- R_g$$
 (III)

Y,  $Y_1$ , and  $Y_2$  each independently designates a linear or branched alkylene radical composed of  $C_2$ - $C_{16}$ .

 $R_7$  designates hydrogen, a linear or branched alkyl radical composed of  $C_1$ - $C_4$ , or a linear or branched hydroxy alkyl radical composed of  $C_1$ - $C_4$ .

R<sub>8</sub> designates an atom of hydrogen or a linear or branched alkyl radical composed of C<sub>1</sub>-C<sub>30</sub>, p, q, and r each independently designates either the value 0 or the value 1, m and n each independently designates a whole number between 0 and 100, x designates a whole number from 1 to 100, Z designates an ion of organic or mineral acid, provided that:

- at least one of the substituent R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, or R<sub>8</sub> designates a linear or branched alkyl radical composed of C<sub>9</sub>-C<sub>30</sub>,
  - if m or n are not equal to 0 then q is equal to 1,
  - if m or n are equal to zero then either p or q is equal to 0.
- 2. Composition according to claim 1, characterized in that the vinyl lactam or alkyl vinyllactam monomer is a compound having structure (IV):

$$CH(R_9) = C(R_{10}) - N = O$$

$$(CH_2)_s$$

where:

s designates a whole number between 3 and 6,

R<sub>9</sub> designates an atom of hydrogen or an alkyl radical composed of C<sub>1</sub>-C<sub>5</sub>,

 $R_{10}$  designates an atom of hydrogen or an alkyl radical composed of  $C_1$ - $C_5$ ,

Provided that at least one of radicals  $R_9$  and  $R_{10}$  designates an atom of hydrogen.

3. Composition according to claim 2, characterized in that the monomer from formula (IV)

is vinyl pyrrolidone.

- 4. Composition according to any of claims 1 to 3, characterized in that  $R_3$ ,  $R_4$ , and  $R_5$ , in formulas (I) and/or (II) each independently designates an atom of hydrogen or a linear or branched alkyl radical composed of  $C_1$ - $C_{30}$ .
- 5. Composition according to any of claims 1 to 4, characterized in that monomer b) is a formula (I) monomer.
- 6. Composition according to any of claims 1 to 5, characterized in that the fact that numbers m and n equal 0.
- 7. Composition according to any of claims 1 to 6, characterized in that the counter ion Z- of the monomers from formula (I) is chosen from among halogenide ions, phosphate ions, the methosulfate ion, and tosylate ion.
- 8. Composition according to any of claims 1 to 7, characterized in that the cationic polymer or polymers according to the invention also contain one or more additional monomers that are preferably cationic or non-ionic.
- 9. Composition according to any of claims 1 to 8, characterized in that the polymer is a terpolymer consisting of:
  - a) one formula (IV) monomer.
- b) one formula (I) monomer in which p=1, q=0,  $R_3$  and  $R_4$  designate a hydrogen atom or an alkyl radical composed of  $C_1$ - $C_5$ , and  $R_5$  designates an alkyl radical composed of  $C_9$ - $C_{24}$ , and
- c) one formula (I) monomer in which  $R_3$  and  $R_4$  designate a hydrogen atom or an alkyl radical composed of  $C_1$ - $C_5$ .
- 10. Composition according to claim 9, characterized in that the terpolymer comprises 40 to

95% by weight of monomer (a), 0.25 to 50% of monomer (b), and 0.1 to 55% of monomer (c).

- 11. Composition according to any of claims 1 to 10, characterized in that the cationic poly(alkyl) vinyllactam polymers are the terpolymers vinyl pyrrolidone / dimethyl amino propyl methacrylamide / dodecyl dimethyl methacrylamidopropyl ammonium tosylate, the terpolymers vinyl pyrrolidone terpolymers / dimethyl amino propyl methacrylamide / cocoyl dimethyl methacrylamidopropyl ammonium tosylate, the terpolymers vinyl pyrrolidone / dimethyl amino propyl methacrylamide / lauryl dimethyl methacrylamidopropyl ammonium tosylate or chloride.
- 12. Composition according to claims 1 to 11, characterized in that the molecular weight by weight of the cationic polymers is comprised between 500 and 20,000,000, preferably comprised between 200,000 and 2,000,000, and even more preferentially comprised between 400,000 and 800,000.
- 13. Composition according to any of the preceding claims, characterized in that the cationic poly(alkyl) vinyllactam polymers are used in a quantity ranging from 0.01 to 10% by weight of the total weight of the composition.
- 14. Composition according to claim 13, characterized in that the cationic poly(alkyl) vinyllactam polymers are used in a quantity ranging from 0.1 to 5% by weight of the total weight of the composition.
- 15. Composition according to any of the preceding claims, characterized in that said protective agent for the keratinous materials is chosen from among UV filters, antiradical agents, antioxidants, vitamins, and provitamins.
- 16. Composition according to the preceding claim, characterized in that said UV filters are chosen from among hydrosoluble, liposoluble, or water-insoluble organic filters, whether siliconated or nonsiliconated, and mineral oxide nanoparticles, the surface of which may

eventually be treated.

- 17. Composition according to the preceding claim, characterized in that said hydrosoluble organic UV filter is chosen from among the group consisting of para-amino benzoic acid and its salts, anthranilic acid and its salts, salicylic acid and its salts, p-hydroxy cinnamic acid and its salts, sulfonic derivatives of benz-x-axole and their salts, sulfonic derivatives of benzophenone and their salts, sulfonic derivatives of benzylidene camphor and their salts, the derivatives of benzylidene camphor substituted by a quaternary amine and their salts, derivatives of phthalydene-camphosulfonic acids and their salts, sulfonic derivatives of benzotriazol, the hydrophilic polymers having, additionally and by their chemical nature, light-protective properties against UV rays, and mixtures of them.
- 18. Composition according to claims 16 and 17, characterized in that said liposoluble organic UV filter is chosen from among: derivatives of para-aminobenzoic acid, such as the esters or amides of para-aminobenzoic acid; derivatives of salicylic acid such as the esters of salicylic acid; derivatives of benzophenone; derivatives of dibenzoyl methane; derivatives of diphenyl acrylates; derivatives of benzofurans; UV filter polymers containing one or more silico-organic residues; esters of cinnamic acid; derivatives of camphor; derivatives of trianilino-s-triazine; the ethylic ester of urocanic acid; benzotriazols; derivatives of hydroxy phenyl triazine; bis-resorcinol-dialkyl amino triazine; and mixtures of them.
- 19. Composition according to claim 18, characterized in that said liposoluble UV filter is chosen from among: octyl salicylate; 2-hydroxy-4-methoxy benzophenone; 4-tertiobutyl 4'-methoxy dibenzoyl methane; octocrylene; 4-methoxy cinnamate of 2-ethyl hexyl, and the compound from the following formula (V):

- 20. Composition according to any of the preceding claims, characterized in that the conditioning agents may be chosen from among the synthesis oils, mineral oils, vegetable oils, fluoridated or per fluoridated oils, natural or synthetic waxes, silicones, cationic polymers other than the poly(alkyl) vinyllactams defined in claims 1 through 12, ceramide type compounds, cationic surfactants, fatty amines, fatty acids and their derivatives, as well as mixtures of these different compounds.
- 21. Composition according to claim 20, characterized in that the synthesis oils are polyolefins of the polybutene type, whether hydrogenated or not, or of the polydecene type, whether hydrogenated or not.
- 22. Composition according to claim 20, characterized in that the cationic polymers are chosen from among those containing units consisting of primary, secondary, tertiary and/or quaternary amine groups that may either form part of the main chain of the polymer, or be carried on a substituent lateral directly connected to the latter.
- 23. Composition according to any of claims 20 to 22, characterized in that said cationic polymer is chosen from among quaternary derivatives of cellulose ether, cationic cyclopolymers, cationic polysaccharides, quaternary polymers of vinyl pyrrolidone, and of vinyl imidazole, and their mixtures.
- 24. Composition according to claim 23, characterized in that said cyclopolymer is chosen

from among homopolymers of diallyl dimethyl ammonium chloride, and the copolymers of diallyl dimethyl ammonium chloride and acrylamide.

- 25. Composition according to claim 23, characterized in that said quaternary derivatives of cellulose ether are chosen from among the hydroxy ethyl celluloses having reacted with an epoxide substituted by a trimethyl ammonium group.
- 26. Composition according to claim 23, characterized in that said cationic polysaccharides are chosen from among guar gums modified by a salt of 2,3-epoxy propyl trimethyl ammonium.
- 27. Composition according to claim 20, characterized in that the silicones are chosen from among the polyorganosiloxanes that are insoluble in the composition.
- 28. Composition according to any of claims 20 to 27, characterized in that the polyorganosiloxanes are non-volatile polyorganosiloxanes chosen from among the polyalkyl siloxanes, polyaryl siloxanes, polyalkyl aryl siloxanes, silicone gums and resins, and polyorganosiloxanes modified by organofunctional groups, as well as mixtures of them.
- 29. Composition according to claim 28, characterized in that:
- (a) the polyalkyl siloxanes are chosen from among:
- the polydimethyl siloxanes with terminal trimethyl silyl groups;
- the polydimethyl siloxanes with terminal dimethyl silanol groups;
- the polyalkyl( $C_1$ - $C_{20}$ )siloxanes;
- (b) the polyalkyl aryl siloxanes are chosen from among:
- the linear and/or branched polydimethyl methyl phenyl siloxanes, polydimethyl diphenyl siloxanes with a viscosity of between 1.10<sup>-5</sup> and 5.10<sup>-2</sup> at 2.5 m<sup>2</sup>/s at 25° C;
- © the silicone gums are chosen from among the polydiorganosiloxanes having an average numerical molecular weight comprised between 200,000 and 1,000,000, used alone or in the

form of a mixture in a solvent;

- (d) the resins are chosen from among resins composed of the units:  $R_2SiO_{2/2}$ ,  $R_3SiO_{1/2}$ ,  $RSiO_{3/2}$ , and  $SiO_{4/2}$ , in which R represents a hydrocarbon group having 1 to 16 carbon atoms or a phenyl group;
- (e) the organo-modified silicones are chosen from among the silicones consisting of in their structure one or more organo-functional groups attached by means of a hydrocarbon radical.
- 30. Composition according to claim 29, characterized in that the silicone gums used alone or in the form of a mixture are chosen from among the following structures:
- polydimethyl siloxane,
- polydimethyl siloxane/methyl vinyl siloxanes,
- polydimethyl siloxane/diphenyl siloxane,
- polydimethyl siloxane/phenyl methyl siloxane,
- polydimethyl siloxane/diphenyl siloxane/methyl vinyl siloxane and the following mixtures:
- mixtures formed using a polydimethyl siloxane hydroxylated at the end of the chain and a cyclic poly-dimethyl siloxane;
- mixtures formed using a polydimethyl siloxane gum and a cyclic silicone; and
- mixtures of polydimethyl siloxanes having different viscosities.
- 31. Composition according to claim 29, characterized in that the organo-modified silicones are chosen from among the polyorganosiloxanes consisting of:
- a) polyethylene oxy and/or polypropylene oxy groups;
- b) amine groups, whether substituted or not;
- c) thiol groups;
- d) alkoxyl groups;

- e) hydroxy alkyl groups;
- f) alkoxy alkyl groups;
- g) alkyl carboxylic groups;
- h) 2-hydroxy alkyl sulfonate groups;
- I) 2-hydroxy alkyl thiosulfonate groups;
- j) hydroxy acyl amino groups.
- 32. Composition according to any of claims 27 to 31, characterized in that the polyorganosiloxanes are chosen from among the polyorganosiloxanes having terminal trimethyl silyl groups, polyalkyl siloxanes with terminal dimethyl silanol groups, polyalkyl aryl siloxanes, mixtures of two PDMS composed of a gum and an oil with different viscosities, mixtures of organosiloxane and cyclic silicones, and organopolysiloxane resins.
- 33. Composition according to claim 20, characterized in that the ceramide type compounds are chosen from among:
  - 2-N-linoleoyl amino-octadecane-1,3-diol,
  - 2-N-oleoyl amino-octadecane-1,3-diol,
  - 2-N-palmitoyl amino-octadecane-1,3-diol,
  - 2-N-stearoyl amino-octadecane-1,3-diol,
  - 2-N-behenoyl amino-octadecane-1,3-diol,
  - 2-N-[2-hydroxy-palmitoyl]-amino-octadecane-1,3-diol,
- 2-N-stearoyl amino-octadecane-1,3,4-triol and in particular N-stearoyl phytosphingosine,
  - 2-N-palmitoyl amino-hexadecane-1,3-diol,
  - (bis-(N-hydroxy ethyl N-cetyl) malonamide),

- N(2-hydroxy ethyl)-N-(3-cetoxyl-2-hydroxy propyl) amide of cetylic acid,
- N-docosanoyl N-methyl-D-glucamine, or mixtures of such compounds.
- 34. Composition according to any of the preceding claims, characterized in that the protective and/or conditioning agents are present at a concentration comprised between 0.001% and 20% by weight in relation to the total weight of the composition, and preferably between 0.01% and 10% by weight.
- 35. Composition according to any of the preceding claims, characterized in that it additionally comprises at least one surfactant chosen from among the anionic, non-ionic, and amphoteric surfactants, and mixtures of them.
- 36. Composition according to claim 35, characterized by the fact that the surfactant or surfactants are present at a concentration comprised between 0.1% and 60% by weight, preferably between 1% and 40% by weight, and even more preferentially between 5% and 30% by weight, in relation to the total weight of the composition.
- 37. Composition according to any of the preceding claims, characterized by the fact that it takes the form of a shampoo, an after-shampoo product, a composition for permanents, straightening, dying, or bleaching the hair, a rinse composition to be applied between the two stages of a permanent or straightening process, and a body wash composition.
- 38. Use of a composition as defined in any of the preceding claims to wash or care for keratinous materials.
- 39. Treatment process for keratinous materials, such as hair, characterized in that it consists of applying a cosmetic composition according to any of claims 1 to 37 to such materials, and then eventually rinsing it off with water.

40. Use of a cationic poly(alkyl)vinyllactam polymer as defined in any of claims 1 to 12 in, or for the manufacture of, a cosmetic composition consisting of at least one protective and/or conditioning agent.

INTERNATIONAL SEARCH REPORT Sonal Application No rei/FR 02/00251 A CLASSINGATION OF SUBJECT MATTER IPC 7 A61K7/06 According to International Patent Classification (IPC) or to both automatics in and IPC B. RELDS SEARCHED Minimum documentation asserting (dassertation gystem followed by classification symbols) A61K COSF IPC 7 Documentation no secret other than manimum documentation to the extent that such documents are included in the fields searched Electronic dass base concerned curing the immensional sourch (name of data base and, where practical electronic used) EPO-Internal, NPI Data, PAJ, CHEM ABS Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the advant passeigns Relevant to dain No. Calegory \* US 4 956 430 A (TAZI MOHAMMED) 11 September 1990 (1990-09-11) claims 1-11 EP 0 680 743 A (OREAL) 8 November 1995 (1995-11-08) claims 1-13 WO DO 68282 A (ISP INVEST INC) 16 November 2000 (2000-11-16) cited in the application Paramathry members are timed in society. Further documents are tisied in the continuation of box C. Special categories of cited documents: These document published after the international fitting date or priority daily and not in conflict with the application but clied to understand the principle or theory underlying the invention. expensive dutating the general state of the last which is not considered to be of particular relevance. Garlist document but published on or after the informations! \*X\* document of particular relevance; the distinct levention cannot be considered norel or cathot be considered to (Ming chase document which may throw double on triofity dain(b) or wisch is clied to establish the publication date of another caution or other special mason (as specified) lively an inventive step when the document is taken alone \*P\* document of personar makeanos; the claimed lower for cannot be considered to trucke an inventive stop while the deciment is combined with one or more other such docu-gness, such combination being obvious to a porson skilled. "O" cocumem retenting to an oral disclosure, use, exhibition or document gubbared prior to the international. Thing date but light man into priority date beared. "A" Occurrent member of the seems palent litting Date of making of the international search report Date of the actual completion of the international search 14/06/2002 7 June 2002 Name and mailing address of the ISA Authorized Officer European Palami Offica, P.B. 5818 Palamilana 2 NL - 2230 HV Ris elle Tel. (-31-70) 540-340, Tx. 31 651 opo nl Faz: (-31-70) 340-3016

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